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Azeotropy: A Limiting Factor in Separation Operations in Chemical Engineering - Analysis, Experimental Techniques, Modeling and Simulation on Binary Solutions of Ester-Alkane

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Additional information is available at the end of the chapter

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Abstract

The presence of azeotropic points in the vapor-liquid equilibria of some solutions is a limiting factor in separation operations by distillation. Knowledge of azeotropy is based on understanding its origins and behavior in relation to the different variables that modulate phase equilibria, and can be used to control the appearance of these singular points. This work studies the phenomenon of azeotropy and presents a practical view based on the study of ester-alkane binary solutions. After considering the principles of vapor-liquid thermodynamics and the special cases of azeotropic points, a detailed description is given of the experimental techniques used to determine these points and also for their thermodynamic verification. Two different but complementary modeling approaches are proposed: the correlation of experimental data and the prediction of azeotropic variables. The first is required to achieve a rigorous design of apparatus and installations, while the second is useful in preliminary design stages. Finally, alternatives to the separation process are studied by simulation. For a practical perspective on these aspects, each section is accompanied by data for ester-alkane solutions, and references are made to applications in the chemical, food and pharmaceutical industries.

Keywords: azeotropy, modeling, experimentation, simulation, ester, alkane

1. Introduction

In general, the matter that makes up the Earth and everything living on it has a heterogeneous nature in relation to the different states (solid, liquid and gas). In the case of liquid solutions, the development of separation technologies is associated with the chemical industry [1, 2], which is a driving force behind it. Any transformation process of matter requires preliminary and/or subsequent steps, which change the composition of the solutions involved. One objective may be to purify the products generated in a reactor, for example, by removing the presence of inert compounds, contaminants, by-products or excess reagents, and even to produce solutions with specific compositions, different to those obtained in the reactor. So, many processes in the chemical industry are essentially combinations of physical separation processes that do not require a chemical reaction.

There are a variety of separation processes known to date [3], but the performance of distillation [4] make it the most important and most used operation in the chemical industry. However, not all solutions can be separated into their simple components by classical multi-step distillation (rectification) techniques. Because of this, advanced methods aimed at resolving the limitations of distillation in relation to specific problems have been developed. Two of the most important complications in the correction of solutions are: (1) the presence of azeotropes and, (2) the proximity of the boiling points of the components in the dissolution (close boiling point). Similar strategies are followed to separate solutions with either of these scenarios, and the main differences between them lie in certain technical details of the design. Some examples are recorded in **Table 1**. Most of the procedures described try to modify the system either by changing the operating conditions (such as in *pressure-swing-distillation*), or by adding an extractant (*entrainer*), although the latter can present some reactivity with some of the components present. Other techniques combine the rectification with other operations based on different physical principles, such as pervaporation or liquid-liquid extraction.

Although important from a practical perspective the problems posed by a “close boiling point” (CBP) do not require complicated theorization. This phenomenon tends to occur in dissolutions involving chemically similar compounds (of the same chemical nature), with a behavior close to ideality. Azeotropy, however, is a complex phenomenon with different modes of presentation for which the complexity increases exponentially with the number of compounds in solution. Many authors have attempted to write about azeotropy [5, 6], while others have focused on making experimental measurements with different solutions and/or compiling the results [7, 8]. However, the current literature is still scarce. It is especially important to clarify the physical causes of the azeotropes, influenced by the situation and their repercussions on process design (with the sequence: experimentation, E-modeling, M-simulation, S), particularly from a practical perspective.

For many years, our research group has conducted experiments on azeotropic systems (see [9–12]), mainly on solutions containing esters, alkanols and alkanes. Experimental developments have also been proposed to determine vapor-liquid equilibria (VLE) [13, 14], and theoretical approaches to model experimental thermodynamic data [14–17] and to assess their quality [18, 19]. In this chapter, the azeotropy is studied from different perspectives which governs the design of some

Enhanced distillation	Particular cases	Mixtures	Entrainer
Azeotropic distillation	Minimum boiling point pressure-swing	Not found	Not found
		THF + water	Non-available
		Methyl ethanoate + methanol	Non-available
	Boundaries bending	Water + ethanol	Non-available
		Hydrochloric acid + water	Sulfuric acid
		Nitric acid + water	Sulfuric acid
	Liquid-liquid extraction	Ethanol + water	Benzene, toluene
		Butanol + water	Self-entraining
		Hydrocarbon + water	Self-entraining
		Pyridine + water	Benzene
	Pervaporation	Ethanol + water Toluene + heptane	Cellulose acetate membrane
Extractive distillation	With volatile solvent	Not found	Not found
	With heavy solvent	Isoprene + pentane	Furfural, acetonitrile
	With salt	Ethanol + water	Acetate-based salts
Reactive distillation	Reactive entrainer without catalyzer	m-xylene + p-xylene Ethanol + water	Tert-butylbenzene Ethylene glycol
	Reactive entrainer catalyzed-promoted	Methyl ethanoate + isobutanol	o-xylene + ionic liquid

Table 1. Advanced distillation techniques with industrial examples and details of the entrainer used.

engineering operations, and more specifically those cited above (E-M-S), actions that the authors have pursued in recent works [20, 21]. Initially, the phenomenon of azeotropy is considered, supported by the basic thermodynamic formulation, in an attempt to understand its origin and sensitivity to changes in the system conditions. The experimental methods available to measure azeotropic points are exposed, their strengths and limitations are discussed, and reference is made to tools [18, 19] to determine data quality. Regarding the modeling, different strategies are used to characterize VLE diagrams and to estimate the presence of azeotropes, with a critical analysis to predict the appearance of singular points. Finally, the information compiled is used in several examples to design azeotropic separation processes, taking into consideration different conditions of ester and alkane solutions.

2. Azeotropy: description of the phenomenon and thermodynamic representation

Etymologically, the term “azeotrope,” coined by the chemists J. Wade and R.W. Merriman [22], comes from the Greek combination of three words “a” (without), “zein” (boiling) and “trope” (change), in other words, to boil without change, referring to a solution for which the variables (p, T, x) remain unchanged, which is the main characteristic of this phenomenon. These authors described the phenomenon of azeotropy when studying the VLE of the

mixture of water + ethanol at atmospheric pressure. They found that at a given composition of liquid solution the mixture cannot separate as the distilled vapor (with composition y) has the same composition as the remaining liquid (with composition x). Thermodynamic formalism establishes the equality $\mathbf{x} = \mathbf{y}$, between the compositions vector of the liquid phase, $\mathbf{x} = [x_1, x_2, \dots, x_n]$ and the corresponding vapor phase, $\mathbf{y} = [y_1, y_2, \dots, y_n]$ of a system with n -components, to indicate the presence of an azeotrope. The previous identity implies that the solution behaves, in relation to the distillation process, as a pure product, giving rise to an unusual situation. The behavior is a result of changes in the structure of the final dissolution (in singular conditions), with a different reorganization compared to the original one of pure products. Changes occur in all non-ideal solutions, although not all of them are azeotropic. We may, therefore, ask, "what is the difference? In the case of azeotropes the average interactions that affect the molecules of different compounds in solution are equivalent, causing the volatilities are the same: All components have the same ability to change into the vapor phase, resulting in both phases (liquid and vapor) having the same composition.

VLE thermodynamics states that the partial pressure of each component, p_i , of a mixture in VLE, is determined by a modified version of Raoult's law:

$$p_i = y_i p = \frac{x_i \gamma_i p_i^0}{\Phi_i} \quad (1)$$

where p is the total pressure of the system, x_i and y_i , the compositions of compound i in the liquid and vapor phase, respectively, $\gamma_i = \gamma_i(x_i, p, T)$ is the activity coefficient of this compound in the liquid phase, $p_i^0 = p_i^0(T)$ the vapor pressure of this component, and $\Phi_i = \Phi_i(y, p, T)$, related to the fugacity coefficient of pure compound i in solution $\hat{\phi}_i$, and as saturated vapor ϕ_i^0 according to the equation,

$$\ln \Phi_i = \ln \left(\frac{\hat{\phi}_i}{\phi_i^0} \right) + \left[\frac{-v_i^0 (p - p_i^0)}{RT} \right] \quad (2)$$

The azeotropic condition established previously, $\mathbf{x} = \mathbf{y}$, combined with Eq. (1), gives place to the following relationship for azeotropic pressure:

$$p = \gamma_i p_i^0 / \Phi_i \quad (3)$$

which must be obeyed for all components of the system. Equation (4) implies the following identity between all components of the mixture:

$$\frac{\gamma_1 p_1^0}{\Phi_1} = \frac{\gamma_2 p_2^0}{\Phi_2} = \dots = \frac{\gamma_i p_i^0}{\Phi_i} = \dots = \frac{\gamma_n p_n^0}{\Phi_n} \quad (4)$$

This equation is important because it can be used as a starting point for several considerations. For example, at low and moderate pressures $\Phi_i \approx 1$ and often at high pressures its value would not vary significantly for different compounds and it is acceptable to assume that $\Phi_i / \Phi_j \approx 1$. Therefore, from Eq. (4) it can be deduced that the presence of an azeotrope is due to γ_i and to p_i^0 , in other words, for there to be an azeotrope in the VLE equations.

$$\gamma_i(T, p, x_i) = p/p_i^o \text{ and } \gamma_j(T, p, x_j) = p/p_j^o \quad (5)$$

must have a real-valued solution. The γ 's are a measurement of the non-ideal nature of the liquid phase owing to the interactional effects in the mixing process and depend upon each specific solution, they cannot be known a priori, but are modeled mathematically. The vapor pressures play an important role and depend only upon the equilibrium temperature which, in turn, depends upon the total pressure of the system studied, see **Figure 1**. For Eq. (4) to be rigorously applied, the parameter Φ_i is required; this is calculated from expressions found in any textbook on the Thermodynamics of Solutions [23]. Its more general expression is:

$$\ln \Phi_i = \left[B_{ii}(p - p_i^o) + (1/2)p \sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \right] / RT \quad (6)$$

where $\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii}$, and the δ_{jk} are easy to deduce; the virial coefficients of the pure compounds B_{ii} and mixtures B_{ji} can be calculated by a correlation process. Adaptation of Eq. (4) to binaries gives:

$$\ln \frac{\gamma_1}{\gamma_2} = \ln \frac{p_2^o}{p_1^o} + B_{11}(p - p_1^o) - B_{22}(p - p_2^o) + p\delta_{12}(y_1 - y_2) \quad (7)$$

There is a clear dependence between the quotients of the activity coefficients and the vapor pressures. Bancroft [24] introduced a rule which, at least graphically is intuitive, that the appearance

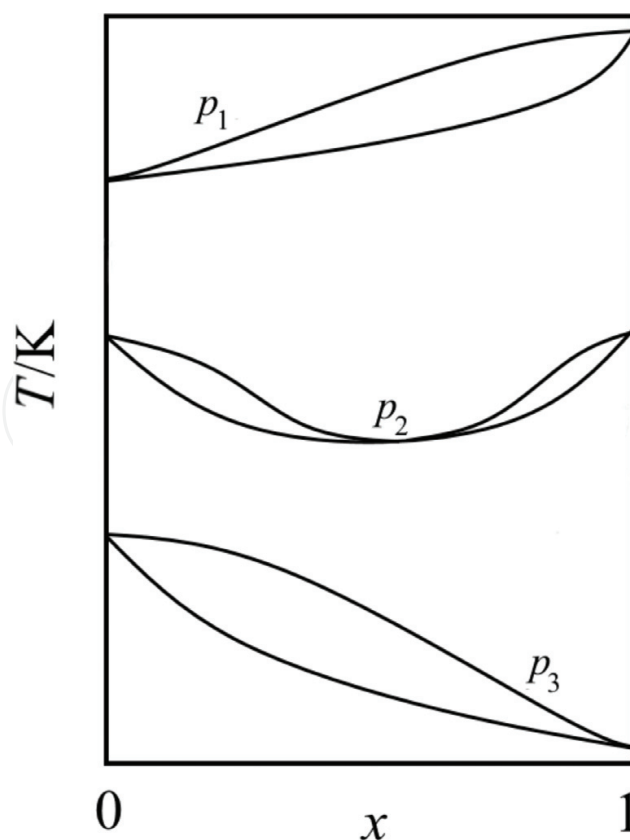


Figure 1. Isobaric-VLE of a binary at different pressures.

of an azeotrope in a homogeneous solution is dependent on the equality of the vapor pressures at a given temperature, ignoring the final summands of Eq. (7). The point of intersection of the vapor pressures is called the *Bancroft point*; although absence of this point does not imply that there is no azeotrope. We insist that one of the most important aspects is to determine the structural behavior of the solution, because the formation of these singular states that identify the azeotropic condition with a pure compound, as mentioned previously, is of significance in the applicability of specific fluids (as occurs in other phase equilibria). This is why it is interesting to define the formation of azeotropes knowing the existence of interactions between different molecules, which can be of attractive nature (favoring the mixing process), or repulsive (impeding it). In the first case, the solution presents a negative deviation of Raoult's law $\gamma_i < 1$, and according to Eq.(4) the p_i^o will be higher than in an ideal solution as would also be the equilibrium temperatures, **Figure 2(a)**. If the net interactional effect is repulsive, $\gamma_i > 1$, p_i^o would be lower to balance out the total pressure. Now, the equilibrium temperatures also diminish creating an azeotrope of minimum temperature, **Figure 2(b)**. Occasionally, the effects of the interactions of a solution are not entirely attractive or repulsive, but their sign varies depending on the state (T, p, x) of the system. In these cases, Eqs. (4) and (5) are satisfied in different regions of the equilibrium plots, and present more than one azeotrope (polyazeotropy), see **Figure 2(c)**. When the solution is affected by strong repulsive effects, the liquid phase becomes unstable and separates into two immiscible liquid phases (liquid-liquid equilibrium, LLE) [25]. High values of the activity coefficients associated with this repulsion favor the formation of azeotropes at a minimum temperature. Sometimes, both phenomena (immiscibility and azeotropy) occur in the same conditions (p, T, x, y), **Figure 2(d)**, giving rise to systems in LLE, VLLE. The types of azeotropes indicated in **Figure 2** for binary solutions also occur in multicomponent systems, although the behavior of the solution is more complex. To illustrate this, **Figure 3** shows the residues, see [3], of some examples of ternaries. The presence of an azeotrope in one of the binaries, **Figure 3(a)**, divides the diagram into two distillation regions by a line that joins the stable node with the unstable node. None of the distillation processes occurring in either of the regions could pass from one to the other, because as they move closer to the region boundary, it will tend to fall to the azeotropic point (stable node). The presence of two azeotropic points would not necessarily change the behavior unless this corresponded to some kind of stable node. Hence, if the azeotrope corresponds to a maximum temperature, it can become an unstable node, **Figure 3(b)**, altering the separation regions.

Ternary azeotropes (those produced in the presence of three solution components) do not necessarily correspond to the minimum points of the diagram; occasionally, **Figure 3(c)**, they

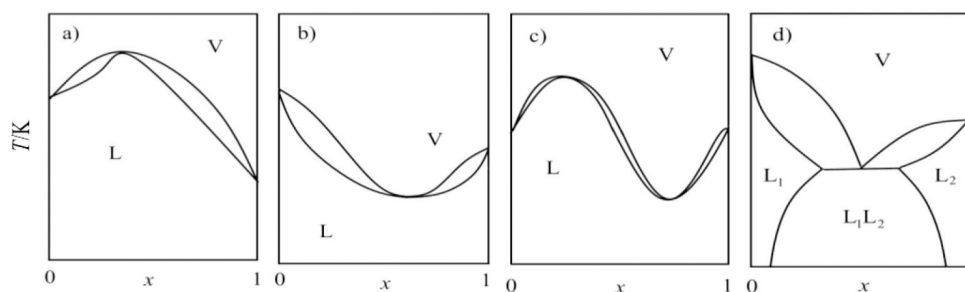


Figure 2. Azeotrope types. (a) Maximum temperature, (b) minimum temperature, (c) polyazeotrope, and (d) non-homogeneous azeotrope. V, vapor phase, L, homogeneous liquid phase, and L_1 and L_2 liquid phases of immiscible system.

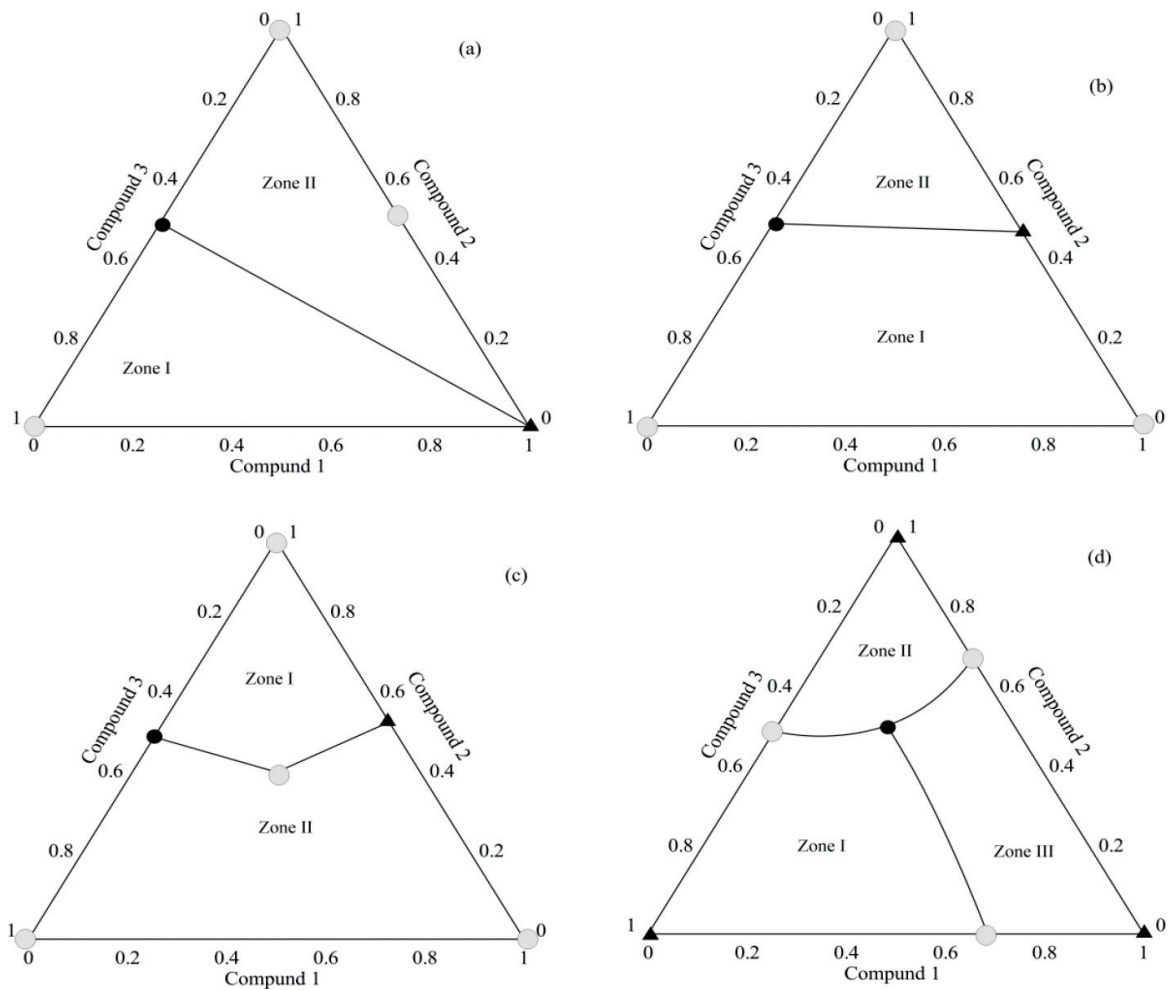


Figure 3. Examples of ternary VLE of azeotropic systems. (●) stable node, (▲) unstable node, (●) saddle-point, (—) separating line. (a) One binary azeotrope, (b) two binary azeotropes, (c) two binary azeotropes and one ternary, (d) minimum temperature ternary azeotrope.

are presented as a saddle-point. However, when they do correspond to the minimum temperature, they also become the stable node for any distillation region. In these cases, the remaining azeotropes also become saddle-points, **Figure 3(d)**.

3. Characterization of azeotropes. Results for ester + alkane solutions

3.1. Experimental techniques for the determination of azeotropes. Details and recommendation

In the experimental characterization of an azeotrope the following parameters or properties must also be specified: (a) composition, (b) boiling point at a given pressure, and (c) the differences between the boiling points of the azeotrope and the most volatile component (positive azeotrope) or that of the component of the lowest boiling point (negative azeotrope). It is usual to specify values for the variables of (a) and (b) to characterize the azeotrope, although the result that establishes (c) should also be given in each case.

Azeotropic points are experimentally determined by several procedures that can be grouped into two categories: direct and indirect. Direct measurements are applied to determine the azeotropic composition inside the apparatus, with the greatest accuracy possible. Experimentalists frequently make mistakes when verifying the precision of the azeotropic coordinates, as the starting products do not always have the desired purity, which distorts the values of the state variables. The commonest example concerns the presence of moisture in the components of a binary system, resulting in the formation of binary or ternary azeotropes with the water; this can even give rise to the appearance of unexpected azeotropes in some systems. Hence, azeotropic experimentation must be rigorous and include a careful rectification procedure. The precise variables of azeotropes can be obtained in a differential ebulliometer [26], such as the one shown in **Figure 4**, with different regions for boiling and condensation, both working to rectify the study mixture, although the temperature on reaching equilibrium must be the same at a given pressure. A recent design for a differential ebulliometer has been proposed by Raal et al. [27].

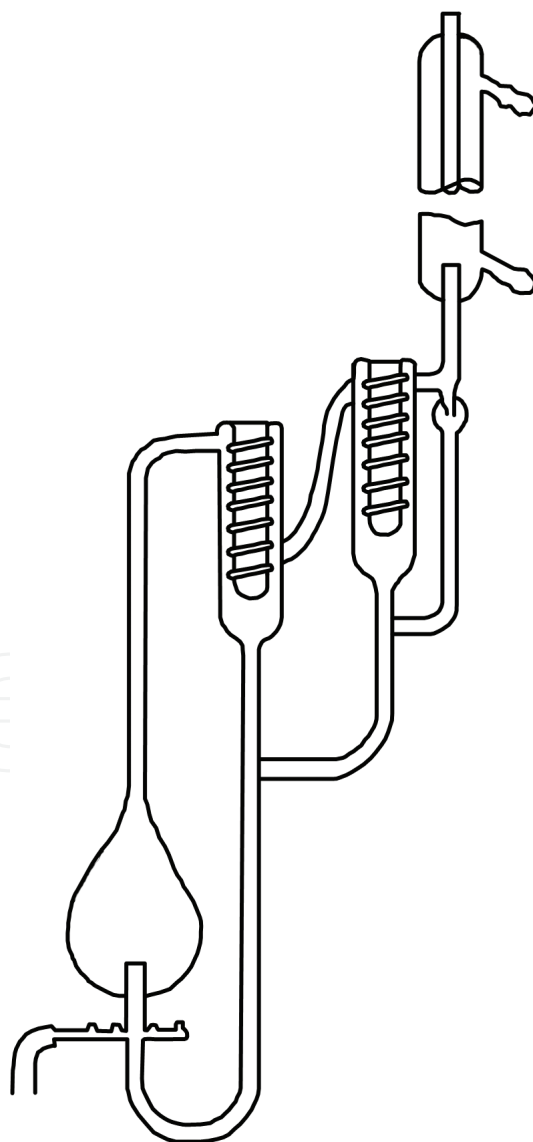


Figure 4. Differential ebulliometer [26].

Several studies are described in the literature [28–30] in which the authors use small or medium-scale installations with distillation columns with a high number of equilibrium phases, operating at total reflux and isobaric conditions. These columns can reach a very similar composition to that of the azeotrope in the reflux, after reaching a steady state. **Figure 4** shows a diagram of an installation **Figure 5**. Packed-tower used for the direct determination of azeotropic points showing details of the installation and auxiliary apparatus. On right, data representations and flow control of these characteristics. To collect the purest fraction possible of an azeotrope a differential ebulliometer is placed adjacent to a distillation column. The pure azeotrope is, therefore, determined in the differential ebulliometer and the difference between the boiling points of the reference compound and that of the azeotrope, with the purpose of estimating the latter.

Figure 5 shows a diagram of the experimental apparatus used in our laboratory to directly measure azeotropic points using a distillation column. This experimental design is useful to characterize the azeotropic points relative to pressure, and to determine the separate regions in systems. The former is carried out by adjusting the pressure of the system to reach a stable temperature at the head of the column, to then take samples of the reflux for analysis. In the case of ternary systems, different starting compositions are used, with the purpose of conducting the experiment in the separate regions. The main drawback of this experimental technique is that the data obtained are not useful for the modeling process, as discrete points are obtained. In any

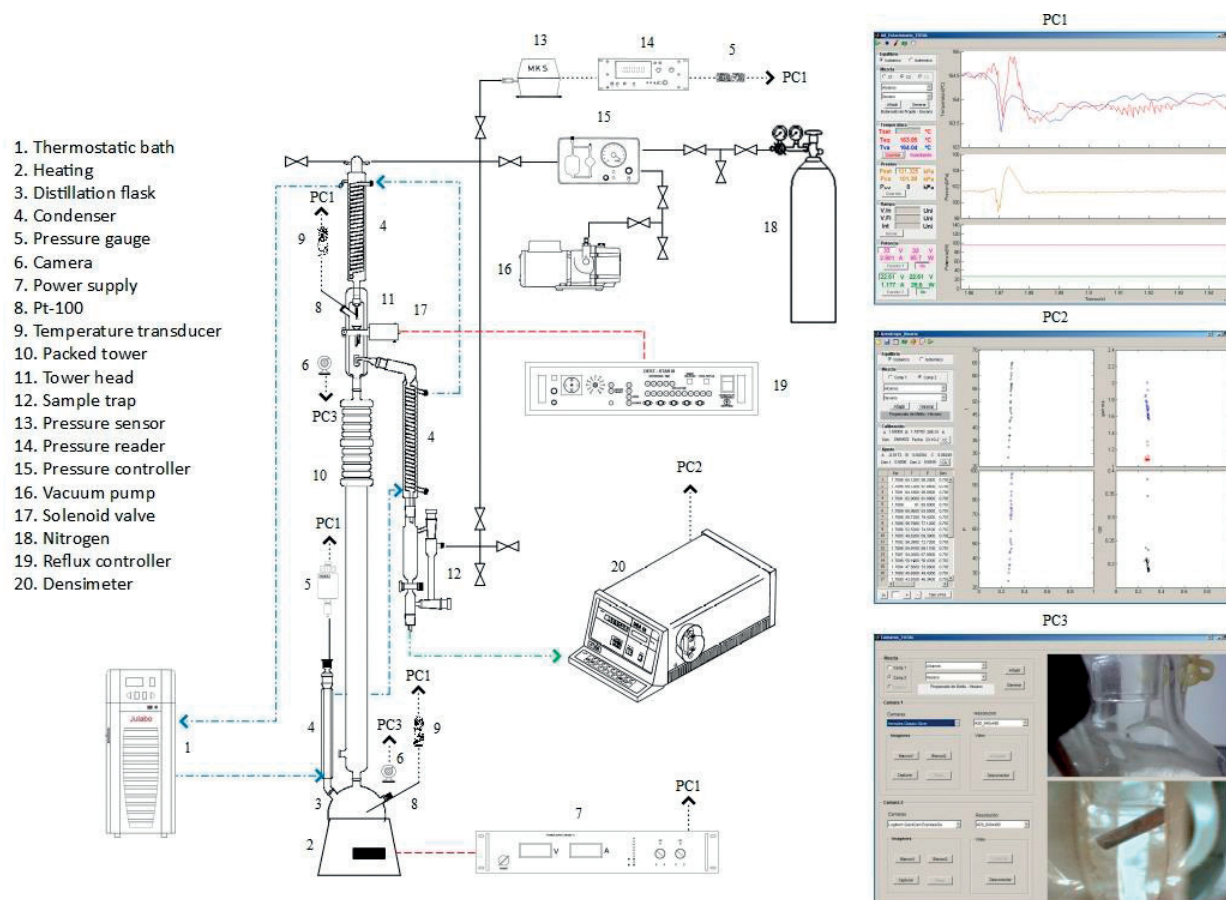


Figure 5. Packed-tower used for the direct determination of azeotropic points showing details of the installation and auxiliary apparatus. On right, data representations and flow control.

case, the azeotropes measured must only be used to complement data available in the complete VLE diagrams.

The indirect technique to determine the coordinates of the azeotropic points consists in interpolating from data determined for the VLE diagram. This is the most widespread procedure [13–15, 26], and the standard one recommended for azeotropes as it describes the entire VLE in given conditions of pressure and temperature. Likewise, an example of the experimental installation to determine VLE data is shown in **Figure 6**, with a small ebulliometer [13, 14] used in our laboratory equipped with a Cotrell pump and a small rectification zone, with temperature differences as specified previously. The samples for binary systems are studied by densimetry/refractometry for ternary systems by gas chromatography. Optimal functioning is achieved by automating the system with suitable software that can carefully control the different variables.

One advantage of the system is that it can obtain a large quantity of data to produce an precise characterization of the VLE. The combination of this technique with the direct method is optimum: the indirect method is used to determine the VLE diagrams of the system in discrete conditions and this information is complemented by azeotropic data at different pressures.

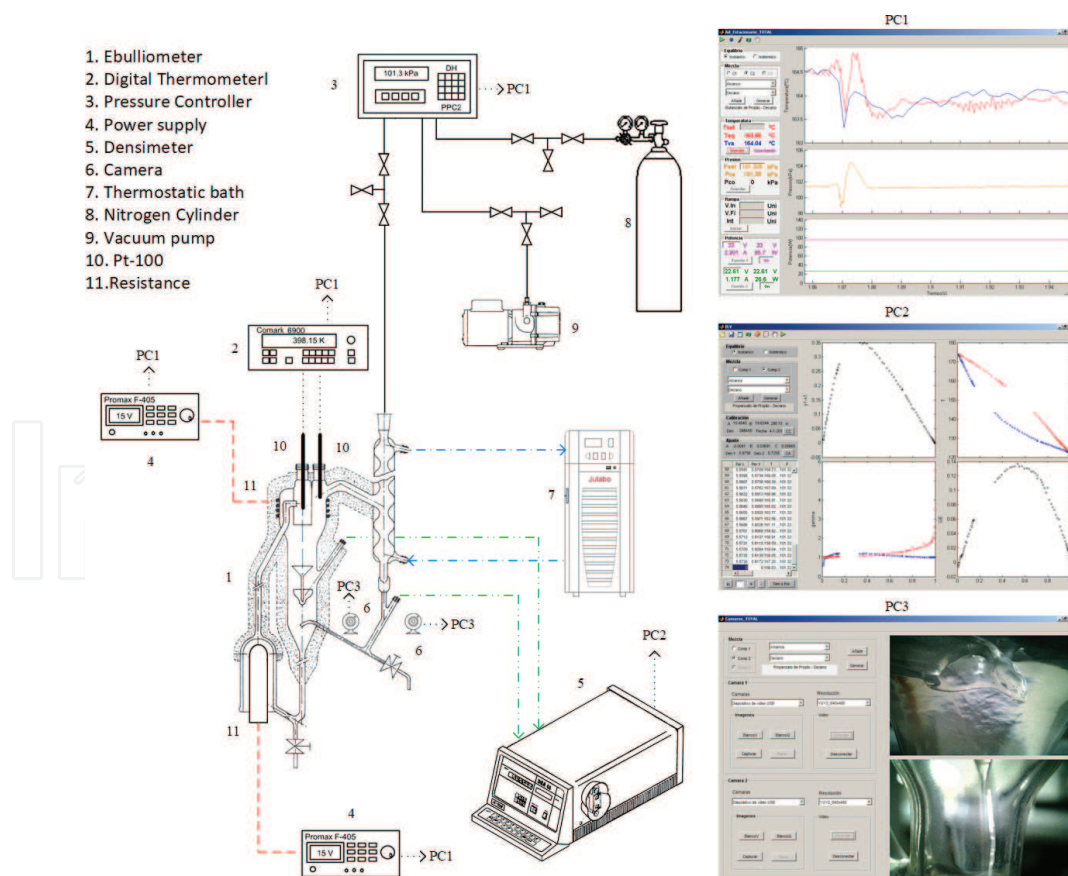


Figure 6. Experimental installation for the experimental determination of VLE, ebulliometer and details of auxiliary equipment.

3.2. Verification of experimental data

The high quality of the starting products and the improvement in the instrumentation and control systems combined with standardization of the experimental protocols, increase the probability of obtaining quality data. In any case, it is important to turn to mathematical-thermodynamic procedures that certify the quality of those data, as these have important repercussions on subsequent operations.

There is a widespread tendency in thermodynamics to establish relationships that verify the scientific coherence between the variables measured, in other words, that establish the *thermodynamic consistency* of the data. Although there are several ways to do this [31, 32], they are of limited scope. In other words, the verification of data must be applied to VLE data before determining the azeotropic coordinates (indirect method). A strategy to check the consistency is based on the following rules:

1. Experimental VLE data are analyzed in graphical form showing the variables measured (x , y , T , p) and those calculated with the thermodynamic formulation, γ_i and g^E . The coherence of these quantities must be illustrated in graphs, otherwise the location of the azeotropes can change. In azeotropic systems, the plot of $(y-x)$ vs. x is important as the intersection of the distribution of points with the x -axis indicates the presence of an azeotrope. In binaries, the coordinates of this point coincide with the minimum or maximum temperature (or maximum or minimum pressures).
2. The experimental data must be modeled to solve most of the consistency tests. Recommendations for this are provided in Section 3 of this chapter.
3. A combination of several consistency tests must be used to confirm the quality of the data and their coherence. The tests as the Areas-test [33] and the Fredenslund-test [34] are recommended, together with a third procedure, although they cannot be used in some cases of azeotropy, such as those appearing in partially miscible systems, **Figure 1(d)**, or polyazeotropes, **Figure 1(c)**. Alternatively, a method proposed by the authors [19], with a more rigorous thermodynamic formulation, could be used.
4. It is also worth mentioning here a method that should be avoided. The method of Herington [35] produces incorrect results by assuming false hypotheses [36] in certain cases. In general, no Area-test should be used as the sole test as they are insensitive to pressure errors [37]. The composition/resolution-test [38], or any other test aimed at exactly obeying thermodynamic relations should also be avoided as they are very limiting.

When applying the consistency test to azeotropic systems some peculiarities must be taken into account. As an example, a brief description is included below of the application of two tests commonly used to analyze VLE data.

- Area-test (Redlich-Kister [33] or other): the method is based on solving the integral,

$$A = \int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} dx_1 \quad (8)$$

which should produce a result close to zero. As mentioned above, the activity coefficients at the azeotropic points are identified with the quotient of the vapor pressures, which provides an additional verification of the data.

- Fredenslund-test [34]: in this case the inconsistency is quantified by the residue generated by this model when reproducing the vapor phase of the VLE system, determining the quality from the difference:

$$\delta y = |y_{\text{exp}} - y_{\text{cal}}| \quad (9)$$

According to this formation, the coordinates of the azeotropic point are only verified with data from the liquid phase:

$$\delta y_1 = \left| x_{1,\text{exp}} - \frac{x_{1,\text{exp}} \gamma_1 p_1^0}{x_{2,\text{exp}} \gamma_2 p_2^0 + x_{1,\text{exp}} \gamma_1 p_1^0} \right| = x_{1,\text{exp}} x_{2,\text{exp}} \left| \frac{\gamma_2 p_2^0 - \gamma_1 p_1^0}{\gamma_2 p_2^0 + x_{1,\text{exp}} (\gamma_1 p_1^0 - \gamma_2 p_2^0)} \right| \quad (10)$$

which should have a value less than 0.01.

In the two cases presented here, the quality of the azeotropic data is linked to the determination of their coordinates by the indirect method. Hence, the azeotropes are verified in the same way as the rest of the data from the VLE series. In order to obtain a procedure that verify the data obtained by the direct method, it is convenient to recur to the test proposed by ours [19], which has the following general expression for a VLE binary (assuming an ideal vapor phase, see [19]):

$$\frac{y_1 - x_1}{y_1(1 - y_1)} = \left(\frac{1}{p} - \frac{v^E}{RT} \right) dp + \left(\frac{h^E}{RT^2} - \sum_{i=1}^2 x_i \frac{\partial \ln p_i^0}{\partial T} \right) dT \quad (11)$$

and imposing the condition of azeotropy:

$$\frac{dT}{dp} = - \frac{\left(\frac{1}{p} - \frac{v^E}{RT} \right)}{\left(\frac{h^E}{RT^2} - \sum_{i=1}^2 x_i \frac{\partial \ln p_i^0}{\partial T} \right)} \quad (12)$$

Integration of Eq. (12), must be carried out numerically as it corresponds to a differential equation of non-separable variables that relates the azeotropic temperature with the pressure of the system. Estimation of the difference between the temperature obtained by Eq. (12) and the experimental temperature is sufficient to verify thermodynamic consistency.

3.3. Azeotropy in ester-alkane solutions

3.3.1. Preliminary analysis

The energetic and volumetric effects of the mixing process of esters and alkanes, due to inter/intra molecular interactions, present net positive values for g^E function, with activity coefficients greater

			C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈	C ₉ H ₂₀	C ₁₀ H ₂₂
			Pentane	Hexane	Heptane	Octane	Nonane	Decane
			T _b ^o = 309.30 K	T _b ^o = 341.88 K	T _b ^o = 371.60 K	T _b ^o = 398.82 K	T _b ^o = 423.97 K	T _b ^o = 447.30 K
C ₂ H ₄ O ₂	Methyl methanoate	T _b ^o = 304.80 K	E(0.558,293.90) ³⁹ D(0.575,294.15) ⁷ D(0.574,294.85) ⁷	E(0.832,302.62) ⁴³ E(0.849,302.65) ⁵⁷ E _Z ⁷	E(0.992,304.69) ⁴⁵ E _Z ¹²	E _Z ¹²	E _Z ¹²	E _Z ⁵⁰
C ₃ H ₆ O ₂	Ethyl methanoate	T _b ^o = 327.50 K	E(0.218,306.50) ³⁹ D(0.215,307.15) ⁷ D _Z ⁷	E(0.703,323.32) ⁴³ E(0.709,323.21) ⁵¹ D(0.669,324.90) ⁷	E(0.988,327.30) ⁷ D(0.973,329.75) ⁷ E _Z ⁵¹	E _Z ¹² E _Z ⁵¹	E _Z ¹² E _Z ⁵¹	E _Z ⁵⁰ E _Z ⁵¹
	Methyl ethanoate	T _b ^o = 330.02 K	E(0.203,307.28) ¹⁷ D(0.295,305.65) ⁷	E(0.683,325.44) ¹⁷ D(0.703,322.65) ⁷ D(0.665,324.80) ⁵²	E(0.962,329.93) ¹⁷ E(0.934,329.6) ⁴⁵	E _Z ¹⁷	E _Z ¹⁷	E _Z ¹⁷
C ₄ H ₈ O ₂	Ethyl ethanoate	T _b ^o = 350.26 K	E _Z ⁴⁰	E(0.339,338.15) ⁴⁰ E(0.343,338.00) ⁴⁶ E(0.343,338.30) ⁵³	E(0.834,349.99) ⁴⁰ D(0.947,350.05) ⁷	E _Z ⁴⁰ E _Z ⁷ E _Z ⁵⁶	E _Z ⁴⁰ E _Z ⁷	E _Z ⁴⁰ E _Z ⁷
	Methyl propanoate	T _b ^o = 352.90 K	E _Z ¹⁴	E(0.279,339.38) ⁴⁷ E(0.216,339.95) ⁷	E(0.844,351.86) ¹⁴ E(0.929,352.75) ⁷	E _Z ⁴⁷	E _Z ¹⁴	E _Z ⁴²
	Propyl methanoate	T _b ^o = 354.00 K	E _Z ³⁹	E(0.283,339.10) ⁴³ E(0.295,336.75) ⁷	E(0.763,352.20) ¹² E(0.736,351.35) ⁷ E(0.786,352.20) ⁵⁵	E _Z ¹² E _Z ⁵⁵	E _Z ¹² E _Z ⁵⁵	E _Z ⁵⁰
C ₅ H ₁₀ O ₂	Ethyl propanoate	T _b ^o = 372.20 K	E _Z ¹⁴	E _Z ⁴⁷ D _Z ⁷	E(0.481,366.61) ¹⁴ E(0.465,366.15) ⁷	E _Z ⁴⁷	E _Z ¹⁴	E _Z ⁴²
	Propyl ethanoate	T _b ^o = 374.69 K	E _Z ⁴¹	E _Z ⁴¹ D _Z ⁷	E(0.423,366.99) ⁴¹ D(0.421,366.75) ²⁹ E(0.423,366.90) ⁴⁸	E(0.973,374.31) ⁴¹ D _Z ⁷	E _Z ⁴¹ E _Z ⁴⁸	E _Z ⁴¹
	Methyl butanoate	T _b ^o = 375.90 K	E _Z ⁴²	E _Z ⁴⁷	E(0.404,367.65) ⁴⁹ D(0.346,368.25) ⁷ E(0.398,368.22) ⁴⁵	E(0.974,375.59) ⁴⁷ D _Z ⁷	E _Z ⁴⁹	E _Z ⁴²
	Butyl methanoate	T _b ^o = 379.30 K	E _Z ³⁹	E _Z ⁴³	E(0.297,368.80) ¹² D(0.346,367.15) ⁷	E(0.872,379.10) ¹²	E _Z ¹²	E _Z ⁵⁰
C ₆ H ₁₂ O ₂	Ethyl butanoate	T _b ^o = 394.60 K	E _Z ⁴²	E _Z ^{47,54}	E _Z ^{7,49}	E(0.637,392.06) ⁴⁷ D(0.646,391.65) ⁷	E _Z ⁴⁹	E _Z ⁴²

			C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈	C ₉ H ₂₀	C ₁₀ H ₂₂
			Pentane	Hexane	Heptane	Octane	Nonane	Decane
			T _b ^o = 309.30 K	T _b ^o = 341.88 K	T _b ^o = 371.60 K	T _b ^o = 398.82 K	T _b ^o = 423.97 K	T _b ^o = 447.30 K
C ₇ H ₁₄ O ₂	Propyl propanoate	T _b ^o = 395.60 K	E _Z ⁴²	E _Z ⁴²	E _Z ⁴² E _Z ⁴⁸	E(0.581,392.88) ⁴² D(0.586,391.95) ⁷	E _Z ^{42,48}	E _Z ⁴²
	Butyl ethanoate	T _b ^o = 399.20 K	E _Z ²⁰	E _Z ^{20,44}	E _Z ²⁰	E(0.553,394.00) ²⁰ D(0.486,393.65) ⁷	E _Z ²⁰	E _Z ²⁰
	Propyl butanoate	T _b ^o = 416.20 K	E _Z ⁴²	E _Z ⁴²	E _Z ^{48,42}	E _Z ⁴²	E(0.713,415.16) ⁴² E(0.726,414.40) ⁴⁸	E _Z ⁴²
	Butyl propanoate	T _b ^o = 419.65 K	E _Z ⁴²	E _Z ⁴²	E _Z ⁴²	E _Z ⁴²	E(0.628,417.12) ⁴²	E _Z ⁴²
C ₈ H ₁₆ O ₂	Butyl butanoate	T _b ^o = 438.61 K	E _Z ⁴²	E _Z ⁴²	E _Z ⁴²	E _Z ⁴²	E _Z ⁴²	E(0.790,438.29) ⁴²

Table 2. Experimental azeotropic coordinates of binary solutions of (an ester + an alkane) at $p = 101.32$ kPa, ($x_{aze}/T_{aze}/K$). Type of technique: E = ebulliometry, D = Distillation, Z = zeotropic system.

than one. This is demonstrated in previous studies [12, 14, 17], together with the presence of minimum boiling point azeotropic points for these solutions; we begin with systems at standard pressure. **Table 2** gives the azeotropic coordinates at $p = 101.32$ kPa available in the literature for alkyl (methyl to butyl) alkanoate (methanoate to butanoate) + alkane (pentane to decane). The esters are arranged according to molecular weight, grouping together the different isomers with similar vapor pressures. Five systems (ethyl methanoate + pentane, methyl methanoate + hexane or heptane, and propyl ethanoate or methyl butanoate + octane) present different results depending of the consulted reference: most of the studies do not report azeotropy but others do.

In most cases, isomeric esters with the same molecular formula have azeotropes with the same alkanes, although this rule is not obeyed by the propyl ethanoate + octane system. An increase in the number of carbons in the ester produces an increase in the appearance of azeotropic points with a lower number of alkanes, resulting from a reduction in the activity coefficients and decreased net effects of the interactions. In esters of greater molecular weight, azeotropes are formed with hydrocarbons of similar vapor pressure as the esters, but with different boiling points for the last esters in the series. For example, propyl butanoate forms azeotropes with nonane, $\delta T_b^0 < 8$ K, but no with octane, $\delta T_b^0 < 17$ K, or with decane, $\delta T_b^0 < 31$ K. In a more extreme case, methyl methanoate forms an azeotrope with hexane, where $\delta T_b^0 > 37$ K. The same phenomenon is described if a hydrocarbon is taken as a reference and the ester is changed. This means that the temperature differences that produce the azeotropy tend to decrease as described in **Figure 7**. The azeotropes arise in solutions of compounds with similar boiling

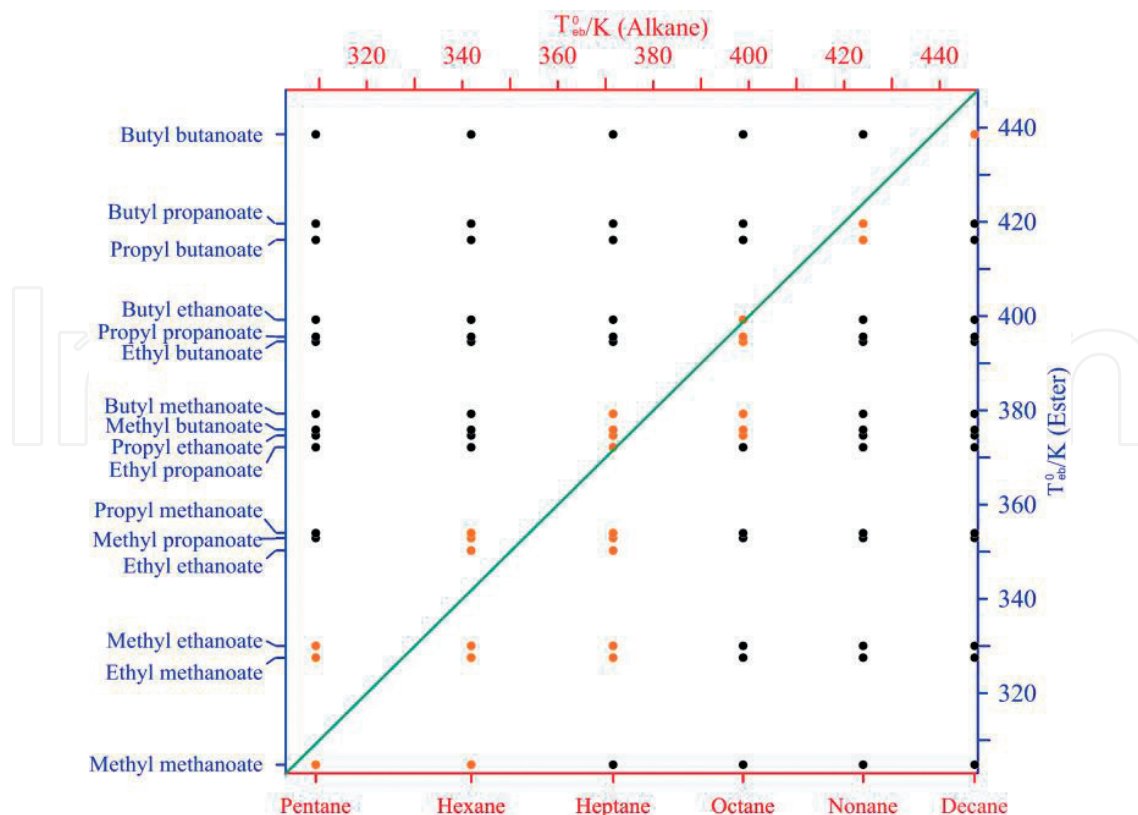


Figure 7. Azeotropes-diagram for ester + alkane mixtures: (●) zeotropic and (○) azeotropic.

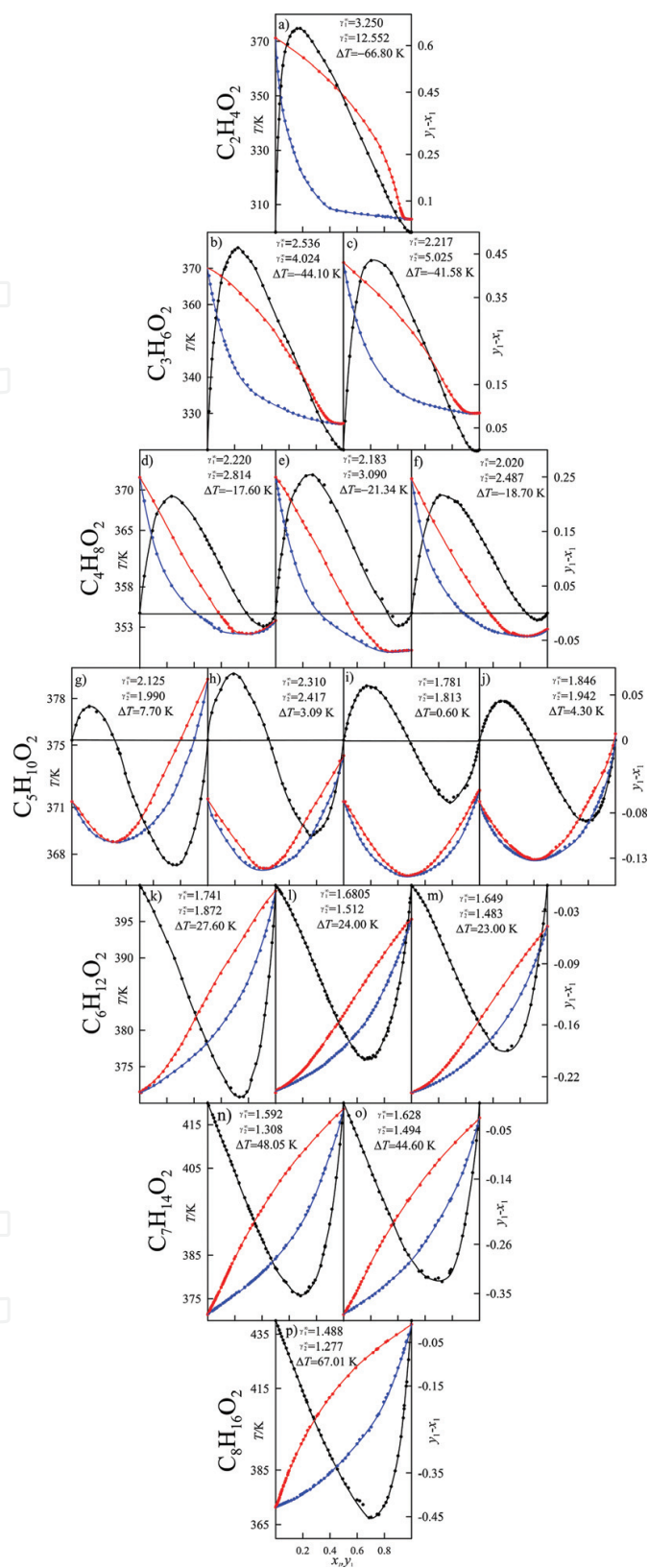


Figure 8. Representation of the VLE of alkyl alkanoate + heptane at 101.32 kPa. Labels indicate the differences of boiling points and the activity coefficients at infinity dilution. (●) T vs. x , (●) T vs. y , (●) $y-x$ vs. x . (a) methyl methanoate, (b) ethyl methanoate, (c) methyl ethanoate, (d) Propyl methanoate, (e) ethyl ethanoate, (f) methyl propanoate, (g) butyl methanoate, (h) propyl ethanoate, (i) ethyl propanoate, (j) methyl butanoate, (k) butyl ethanoate, (l) propyl propanoate, (m) ethyl butanoate, (n) butyl propanoate, (o) propyl butanoate and (p) butyl butanoate.

points arranged near to the diagonal, from the bottom left corner (methyl methanoate + pentane) to the top right (butyl butanoate + decane).

The distance from the azeotropic points to the diagonal becomes shorter as the boiling points of the products increase, and it is deduced that the probability that an ester forms an azeotrope with a given alkane varies with the molecular weight of that ester, although this is reflected in the VLE diagram of the system. **Figure 8** shows the VLE curves of the solutions composed of the different esters and heptane. The difference between the liquid and vapor curves, which shows the volatility, is greater in systems with a smaller ester. This difference only significantly decreases with an increase in the molecular weight of the ester, but does not significantly change with the isomers. This is a result of a decrease in the non-ideality of the liquid phase ($\gamma \approx 1$) in solutions of the larger esters. This change makes it possible to find azeotropes in esters with four carbons, but not in esters with six carbons, in spite of similar differences between the boiling point of the esters and heptane. In ester solutions with five carbons, important differences are observed between isomers, and the azeotrope is found in the equimolar composition in the ethyl propanoate + heptane solution, and in the other cases slightly displaced toward greater alkane compositions. In other words, when the vapor pressures of the compounds are very similar, slight differences in the activity of compounds (e.g., those derived from small steric effects caused by isomerism), have significant repercussions on the equilibrium diagrams. For example, the non-ideality of the solution produces a flat region in the diagram of the solution with methyl methanoate. This does not appear in the mixture with butyl butanoate, which has a practically ideal nature.

Taking all this into consideration, it is important to study the behavior of the azeotropic phenomenon within the families of esters. **Figures 9** and **10** show the matrix with diagrams of y vs. x for solutions of (an alkyl ethanoate + an alkane) and (an methyl alkanoate + an alkane), respectively. In both cases, the presence of azeotropic situations can be observed to shift from the mixtures of more volatile compounds to the less volatile ones, with the last azeotrope appearing in the solution of butyl ethanoate + octane in **Figure 9**, and in the solution of methyl butanoate + heptane in **Figure 10**. The increased chain length of the alkyl ester, **Figure 9**, systematically displaces the azeotrope to regions with a smaller ester

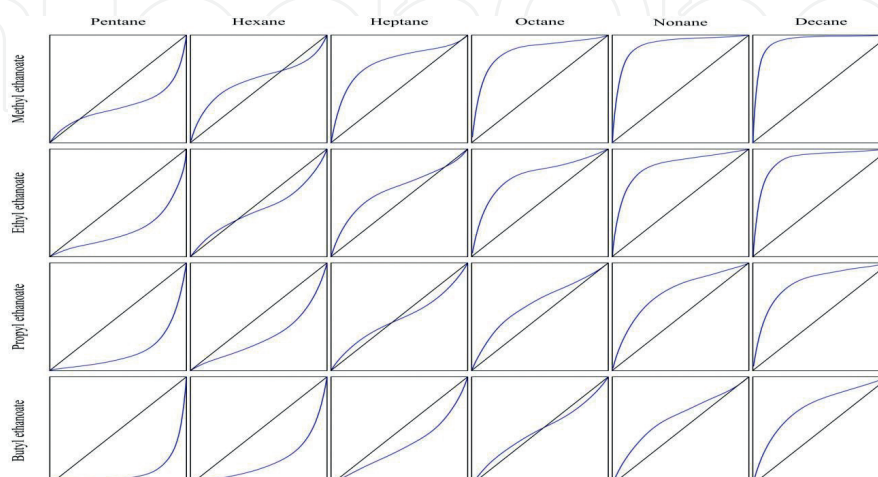


Figure 9. Plot of y vs. x (—), for the VLE at 101.32 kPa of binaries (an alkyl ethanoate + an alkane).

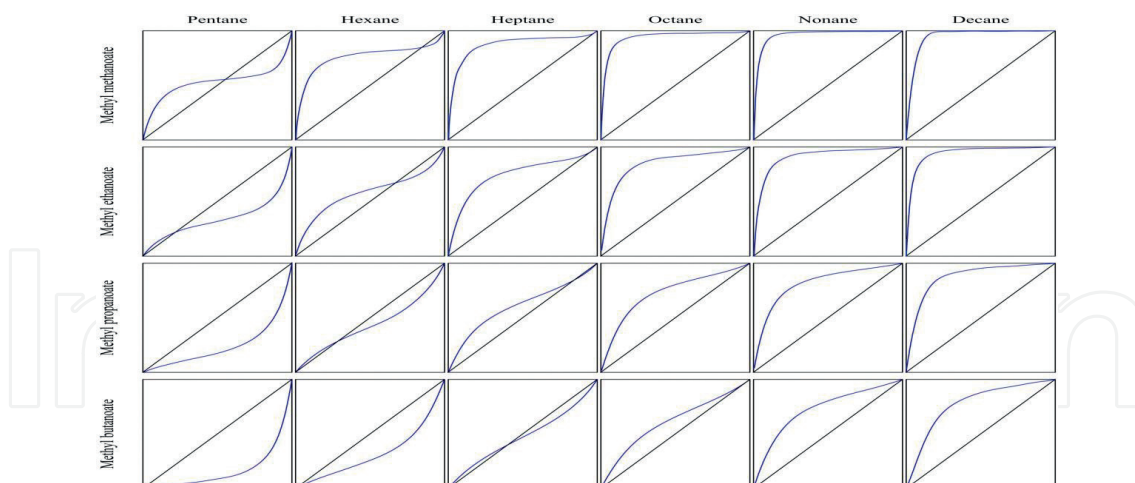


Figure 10. Plot of y vs. x (—), for the VLE at 101.32 kPa of binaries (methyl alkanoates + alkanes).

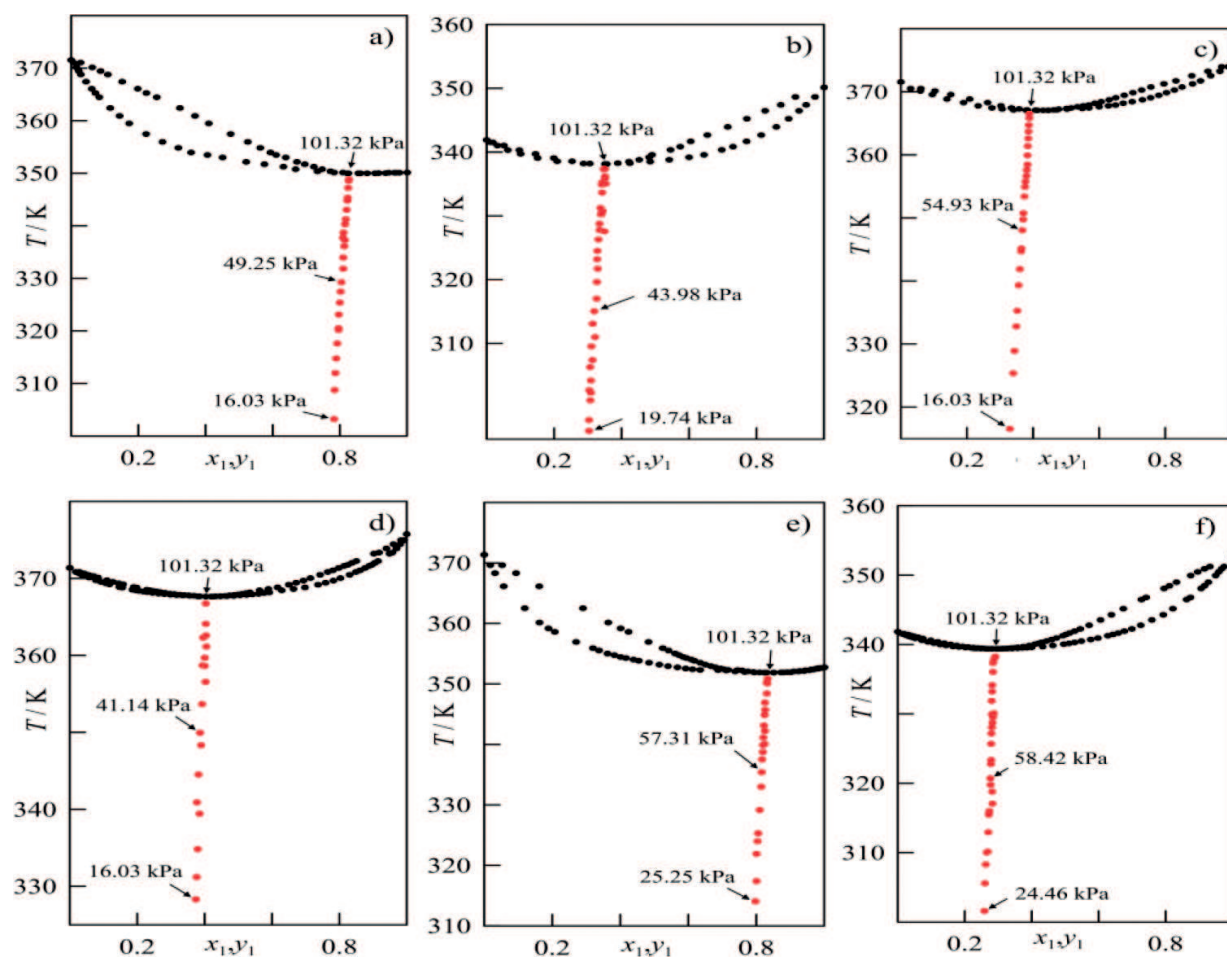


Figure 11. Sensitivity of the azeotropic coordinates to pressure in ester + alkane solutions. (a) Ethyl ethanoate + heptane, (b) ethyl ethanoate + hexane, (c) propyl ethanoate + heptane, (d) methyl butanoate + heptane, (e) methyl propanoate + heptane, (f) methyl propanoate + hexane.

composition. This effect can also be observed with increased alkanoic chain length of the ester, **Figure 10**. By contrast, increases in the size of the alkane cause a shift toward a higher ester composition in both cases.

3.3.2. Changes in azeotropes with pressure

The pressure of the system is a determining factor in the azeotropes formation, so it is important to determine how this magnitude affects the presence of azeotropic points. **Figure 11** shows the case of several azeotropic points determined by distillation for a set of ester + alkane systems, following indications described previously. In all cases, the composition of the azeotrope shifts toward greater alkane compositions as the pressure is reduced. The main reason for this is that the vapor pressure of the ester diminishes more slowly than that of the alkane, which increases the volatility of the hydrocarbon. The slope corresponding to the change in azeotropic composition is similar since the slope of the vapor pressure does not vary greatly between compounds from the same family. In spite of this, the methyl butanoate + heptane system, **Figure 11(d)**, presents a gentler slope, since the differences in vapor pressure between both compounds do not change significantly with temperature.

4. Modeling of azeotropic systems. Correlation and prediction

4.1. Correlation of vapor-liquid equilibria according to the gamma-phi approximation

The modeling of systems presenting azeotropes is not different from that used for any other system in vapor-liquid equilibrium. In order to do this, the following models must be defined:

1. One for the vapor pressure, $p_i^o = p_i^o(T)$.
2. One for ϕ_i $\Phi_i = \Phi_i(\mathbf{y}, p, T)$.
3. A model for the activity coefficients: $\gamma_i = \gamma_i(\mathbf{x}, p, T)$.

The relationship between vapor pressures and temperature is established by Clapeyron's equation [23], although it is standard practice to use other empirical equations such as those of Wagner or Antoine [25]. The parameter Φ_i , defined in Eq. (2), depends on the fugacity coefficient of compound i as saturated vapor phase and in solution. For the calculation, state equations can be used that may be different depending on if they are applied to the liquid or vapor phase.

The activity coefficients are inherent to the formation of the solution and are related to the interactions occurring therein. The phenomenological description of the fluid material is still not precise, although there are some models for which the formulation takes into account the molecular interactions that generate the macroscopic properties. In practice, depending on the theory of the model chosen, some experimental data are required for their accurate representation. For the *gamma-phi* method, models are written for the function of Gibbs excess energy as $g^E = g^E(\mathbf{x}, p, T)$, and the dependence on γ_i is related to its partial molar properties [23]:

$$\gamma_i = \exp \left\{ \left[g^E + \left(\frac{\partial g^E}{\partial x_i} \right)_{p, T, x_{j \neq i}} - \sum_k x_k \left(\frac{\partial g^E}{\partial x_k} \right)_{p, T, x_{j \neq k}} \right] / RT \right\} \quad (13)$$

The model most used to date is NRTL [57]:

$$g^E = RT \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \quad \text{where } G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad \text{and } \tau_{ji} = f(x, T) \quad (14)$$

Our research group has used a polynomial model [14–17], with the general expression:

$$g_{n,N}^E = \sum_{i_1 i_2 \dots i_{n-1} \in C(n,n-1)} g_{n-1,N}^{E(i_1-i_2-i_3 \dots -i_{n-1})} + Z_n \cdot P_N \quad (15)$$

Where n is the number of components present, N the maximum interaction order, $g_{n-1,N}^{E(i_1-i_2-i_3 \dots -i_{n-1})}$ the excess Gibbs function of all the subsystems of inferior order that are present in the system and the product $Z_n \cdot P_N$ is a polynomial made up of multiple products of $(z_1 z_2 \dots z_n)$ and a polynomial in z_i :

$$Z_n = z_1 z_2 \dots z_n = T_n = \frac{\prod_{i=2}^n k^{ij} \prod_{i=1}^n x_i}{\left[x_1 + \sum_{j=2}^n k^{ij} x_j \right]^n}, \quad P_N = \sum_{j=0}^N P_j z_n^j \quad (16)$$

For a binary or ternary solution, the model (Eq. (15)) can be written, respectively, as:

$$g^{E(i-j)} = z_i z_j \sum_{k=0}^{N-2} g_k^{(i-j)} z_i^k \quad (17)$$

$$g_{3,4}^E = g_{2,4}^{E(1-2)} + g_{2,4}^{E(1-3)} + g_{2,4}^{E(2-3)} + z_1 z_2 z_3 (C_0 + C_1 z_1 + C_2 z_2) \quad (18)$$

with the possibility of extending this rule to any number of components. This model has been used to represent the behavior of many binary and ternary systems and has provided excellent results when used in combined correlation procedures of all the properties. This combined modeling method, adapted to suit to each case, was applied to binaries composed of esters and alkanes [10–17, 39–56]. The two following models: NRTL [57] and the Eq. (17) were used. Several of the systems modeled present azeotropy, so the results obtained are described briefly below. In many cases, the two models reproduce the VLE diagram with similar errors. An example is that shown in **Figure 12(a)** for the solution methyl methanoate + pentane, with iso-101.32 VLE data [39]. Slight differences can be observed in the azeotropic coordinates (T_{az}/K ; x_{az}) calculated by each model [the proposed model (17) estimates the coordinates to be (293.8; 0.54), while the NRTL model gives (293.7; 0.57)]. However, Eq. (17) is better at predicting the remaining properties and, therefore, guarantees a better global capacity of representation (see details in [39, 41]). Occasionally, the NRTL model does not adequately represent the VLE behavior of azeotropic systems, especially when the parameters are obtained in a combined correlation process as

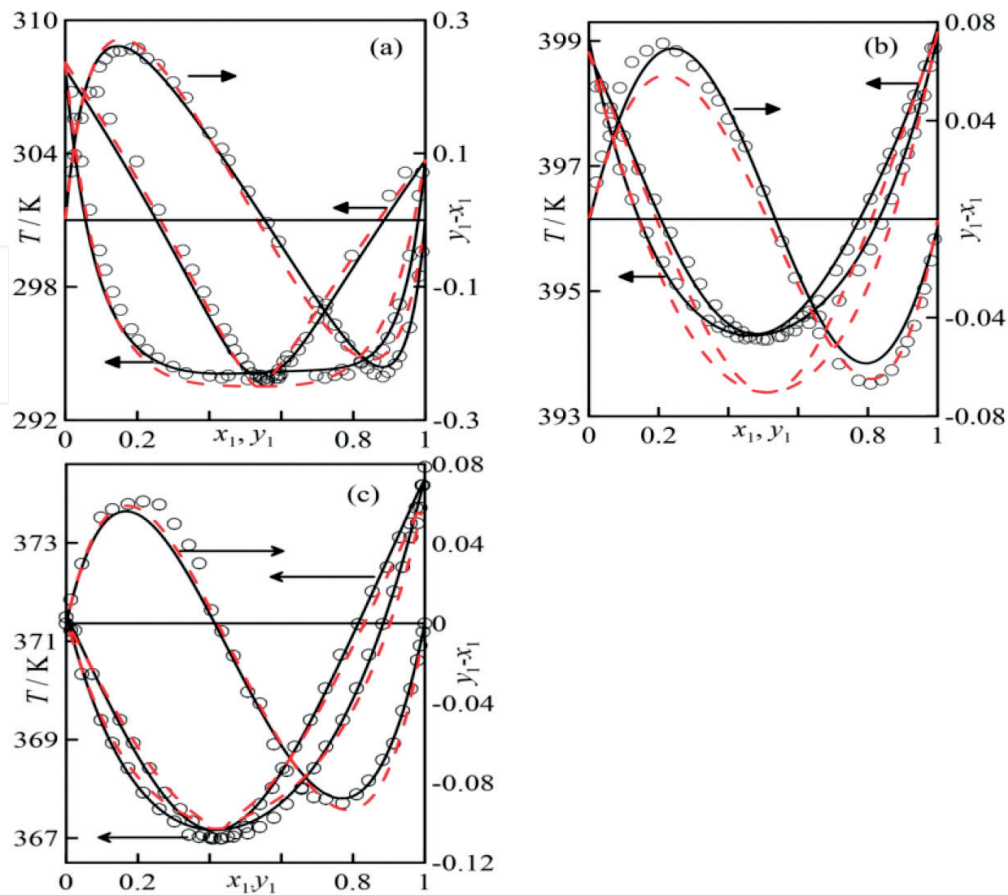


Figure 12. Modeling examples of azeotropic systems using correlative models for: (a) methyl methanoate(1) + pentane(2), (b) butyl ethanoate(1) + octane (2), (c) propyl ethanoate(1) + heptane(2). (—) Eq. (17), (---) NRTL, Eq. (14).

recommended here (see [58, 59]). For example the solution butyl ethanoate + octane [20], and reproduced in **Figure 12(b)**, for which NRTL estimates $T_{az} = 393.4$ K, while model (17) gives $T_{az} = 394.1$ K, close to the experimental value of $T_{az,exp} = 394.0$ K.

In some cases, a considerable amount of data is modeled together. When these extend over a broad range of pressures and temperatures the ability of both models to accurately reproduce the azeotropic coordinates, or any other property, diminishes. In other words, the resolution capacity in the calculation of coordinates, at a given p , becomes smaller as the range of estimation increases. This case was studied [60] for the solution propyl ethanoate + heptane, where VLE data were available for temperatures between 273 and 373 K. Estimations for the two models, for iso-101.32 kPa VLE, are shown in **Figure 12(c)**, which shows that the azeotropic temperature calculated for the two models (367.17 K with our model and 367.19 K with NRTL) is slightly higher than the experimental value (367.0 K). These results are considered here to be positive. In conclusion, from observations made from the modeling described in numerous articles [10–17, 39–41], the model (17) appears to be recommendable to correlate VLE data and hence, to estimate azeotropic conditions. Either model can be used for the individual correlation of VLE data, although the modeling obtained should not be used to extrapolate azeotropic coordinates to conditions different from the experimental conditions.

4.2. The prediction of azeotropes by activity coefficients. Application to ester + alkane solutions

When experimental VLE data are not available, azeotropic points are estimated using predictive procedures. In the field of chemical engineering, the UNIFAC model by Gmehling et al. [61] (referenced as UNIFAC-DM), mainly designed for phase equilibria and some derived properties, is well known. Nonetheless, advances in the molecular sciences have helped to understand the intrinsic behavior of fluids in greater depth, with more solid phenomenological bases. This is the case of the quantum chemistry-based COSMO-RS model [62], which is able to estimate a significant number of properties of solutions. This chapter compares the results obtained after applying the two models to ester-alkane binaries, enabling us to establish certain criteria for their use.

Figure 13 represents the relative errors obtained with each of models in the estimation of azeotropic points of ester-alkane systems. The plot is constructed with color gradient according to the magnitude of the error (white cells indicate non-azeotrope). The error measurement is evaluated as:

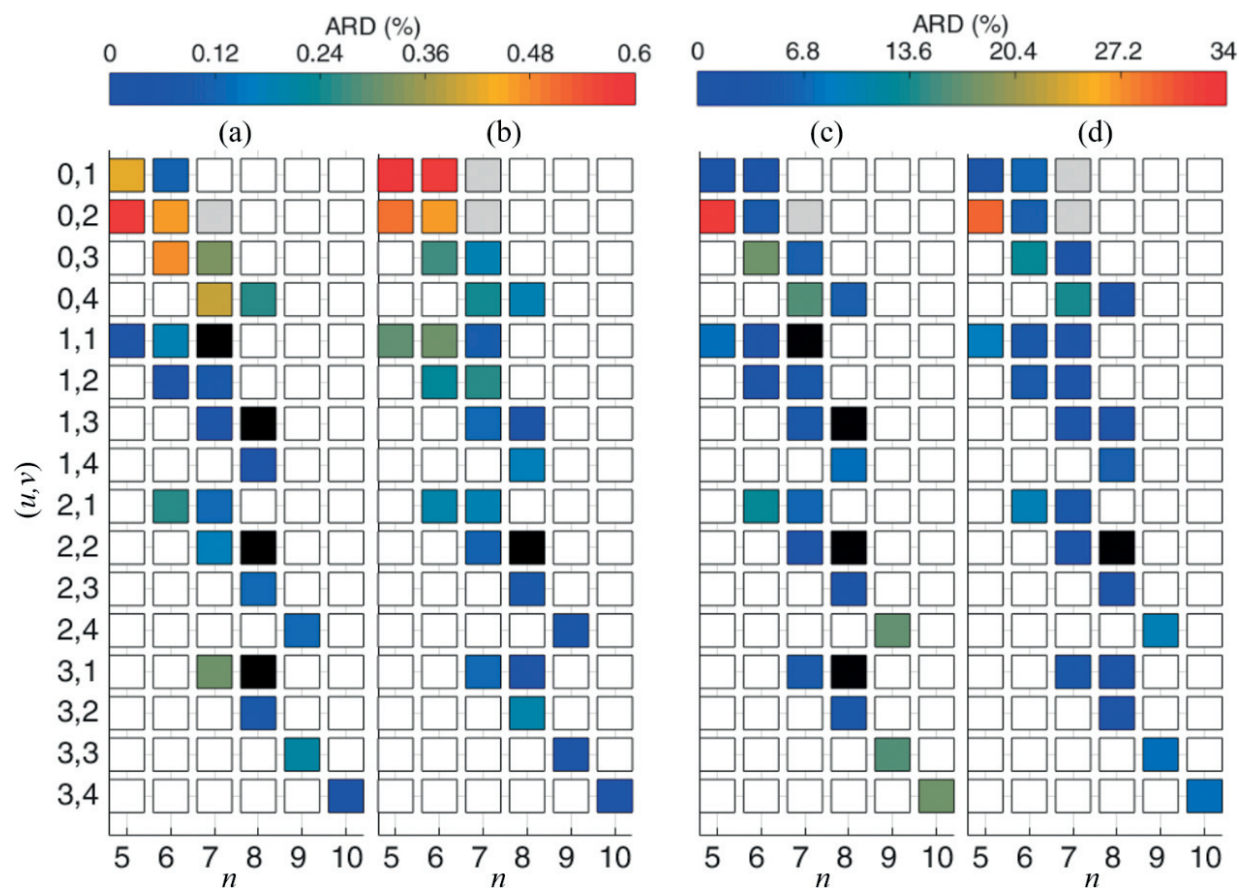


Figure 13. Matrices of estimated ARD for azeotropic coordinates of ester + alkane: $C_{u-1}H_{2u+1}COOC_vH_{2v+1} + C_nH_{2n+2}$. Errors in composition with UNIFAC-DM (a) and COSMO-RS (b); and in temperature using UNIFAC-DM (c) and COSMO-RS (d). ■ Model fails to estimate the azeotrope; ■ Model wrongly considers the system as azeotropic.

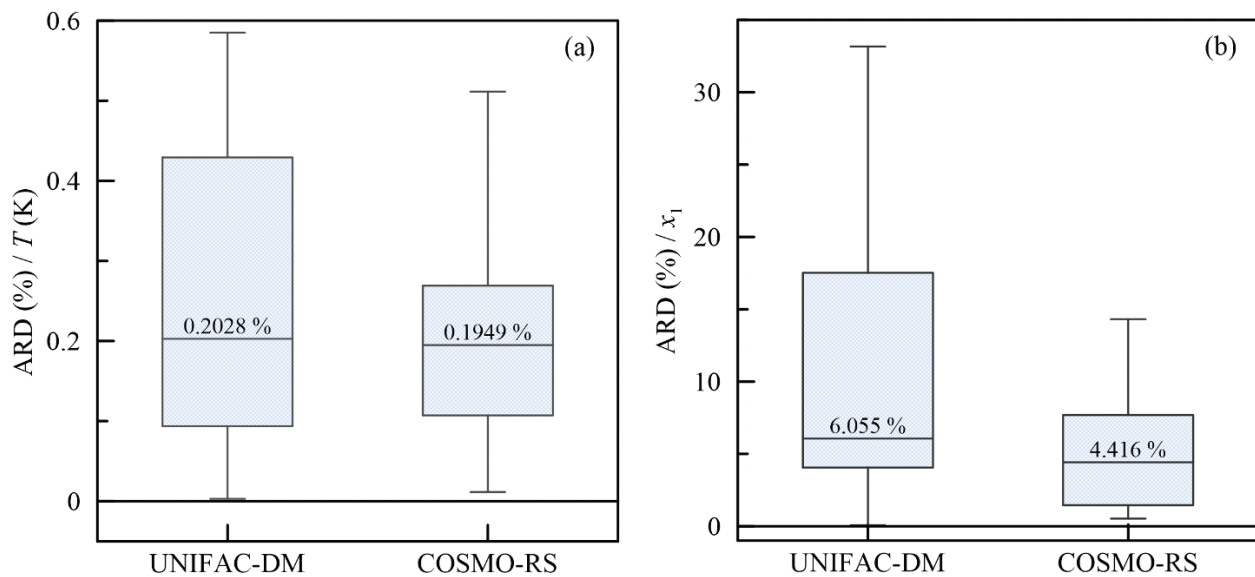


Figure 14. Plot of boxes and whiskers of ARD distribution on the estimation of temperature (a) and composition (b) of the azeotropes obtained with the models UNIFAC-DM and COSMO-RS.

$$ARD_f = \left| \frac{f_{\text{exp}} - f_{\text{est}}}{f_{\text{exp}}} \right| \cdot 100 / f_{\text{exp}} \quad \text{where } f \equiv x_{\text{az}} \text{ or } T_{\text{az}}/K \quad (19)$$

colored according to the scale shown in **Figure 13**. In general, an acceptable description is observed for both models for the azeotropic systems studied, although both are less effective at estimating the composition, $\max(ARD_x) = 33\%$, than the equilibrium temperature of the azeotrope, $\max(ARD_T) = 0.6\%$. However, there are some differences in the qualitative description produced by both models. Hence, UNIFAC-DM does not estimate an azeotrope in the systems methyl ethanoate + heptane, propyl ethanoate + octane and methyl butanoate + octane, but considers the system ethyl methanoate + heptane to be azeotropic, which is regarded as zeotropic in the literature. With regards to the COSMO-RS model [61], all the systems described in the literature as azeotropic qualified to be so by the model, with the exception of methyl methanoate + heptane and ethyl methanoate + heptane, which are qualified as azeotropic (see **Figure 13**) when experimentally they are not obtained at the pressure studied. In summary, estimation of the azeotropic coordinates is slightly more accurate when using the COSMO-RS model than the UNIFAC-DM model, as can be observed in the box-and-whiskers diagrams of **Figure 14**. Although both models give a similar mean error, the errors presented by estimations obtained with COSMO-RS have a significantly smaller interquartile range than those obtained with UNIFAC-DM; in other words, they have less dispersion. The same pattern can be observed in the estimation of compositions but with the additional factor that the mean error with the COSMO-RS model is also smaller.

In the preliminary design of separation equipment or *screening* procedures involving ester + alkane systems it is recommended to use COSMO-RS rather than UNIFAC-DM to predict the azeotrope. This is not because of the quantitative difference between the estimations, but because of the qualitative improvement obtained with the former model in several of the cases

The pressure in the second column is extremely low, which is difficult to get in practice, but is established here to emphasize the characteristics of *pressure-swing-distillation* operation. As can be observed in **Figure 16**, the difference in pressure between the columns significantly displaces the coordinates of the azeotropic point, as estimated by Eq. (17). So, in the first column there is a partial separation of the solution, with the alkane, of high purity, collected in the bottom. The composition obtained in the head of the atmospheric column that feeds the second tower, **Figure 15**, was established between the azeotropic composition at each pressure, in order to optimize the number of stages.

The influence of the model used on the design was studied [21], and the most significant discrepancy that arises when changing the model occurs in the composition and temperature profiles in the inside of the column as shown in **Figure 17**, where important differences can be found. Use of the proposed model can therefore, guarantee reproduction of the real behavior of the apparatus.

5.2. Separation of the binary ethyl butanoate + octane by extractive distillation

In the previous case, it was proposed to reduce the pressure in order to separate the azeotropic solution. Alternatively, an extractant (*entrainer*) can be used to displace or destroy the azeotrope. This can be illustrated by separating the azeotropic solution ethyl butanoate(1) + octane(2) ($x_{1,az} = 0.63$, $T_{az} = 392$ K a $p = 101$ kPa). For the preliminary design of this type of process a suitable *entrainer* must be chosen. In the absence of experimental data, theoretical models are chosen to establish the feasibility of the process. As possible *entrainers* for the binary selected, two compounds were chosen from the same families (ester and alkane) but with some structural differences, with greater molecular weights and, therefore, higher boiling points: (1) decane (2) butyl

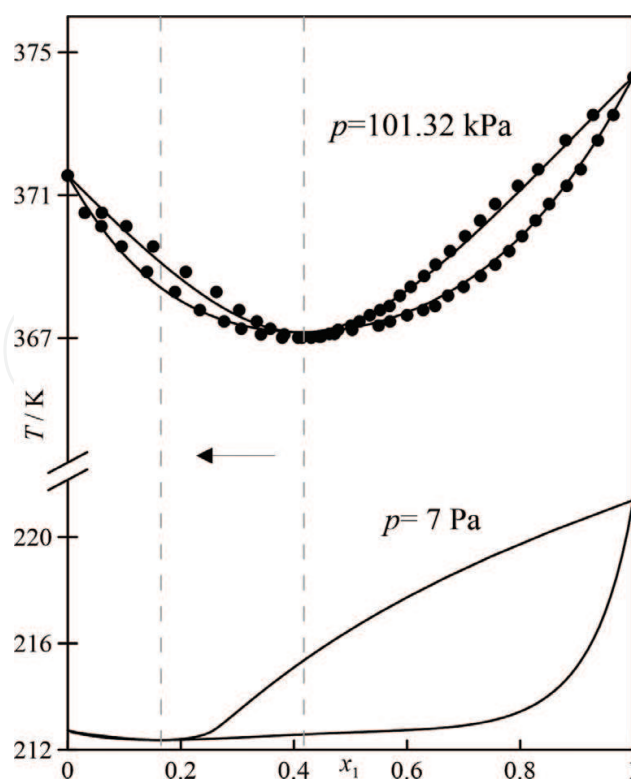


Figure 16. Representation of T vs. x, y of propyl ethanoate(1) + heptane(2). (●) Experimental values, (—), Eqs. (8–10).

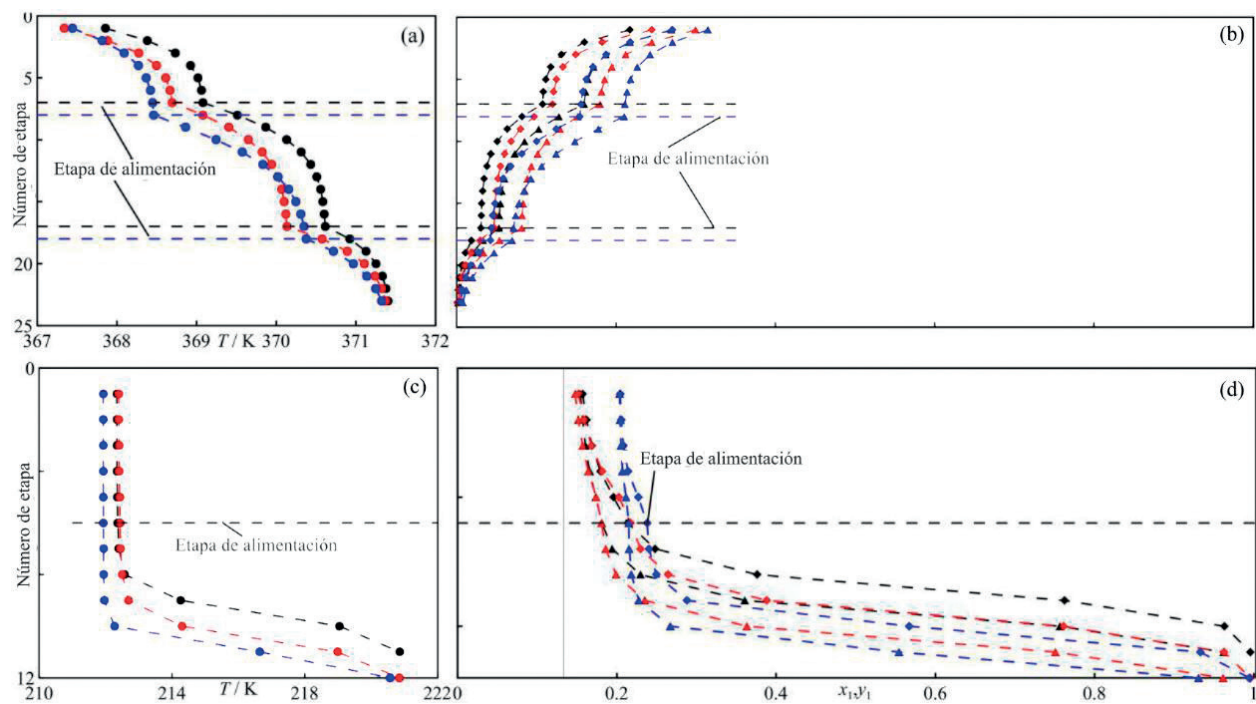


Figure 17. Profiles of temperature (a) and composition (b) for the first and second tower, obtained with Eqs. (17) (---), NRTL (---), and UNIFAC (---). (●) T/K , (▲) liquid phase composition, x ; (□) vapor phase composition, y .

butanoate. Taking into consideration the comments made in Section 3.2 of this chapter, the results obtained by UNIFAC-DM and COSMO-RS are compared being the representation of this azeotropic system more accurate with the former model. On the other hand, the ester + alkane binaries resulting from combining compounds of the mixture with potential solvents give rise to zeotropic systems of high relative volatility, with both models producing good estimations.

The final selection of one solvent or the other is based on the dynamics of the ternary system formed in the column, from analysis of the residual curves, **Figure 18**. The results obtained show that decane is the best option, since the residual curves rapidly veer toward the line $x_1 = 0$, facilitating the subsequent separation. Introduction of the solvent in the process and the

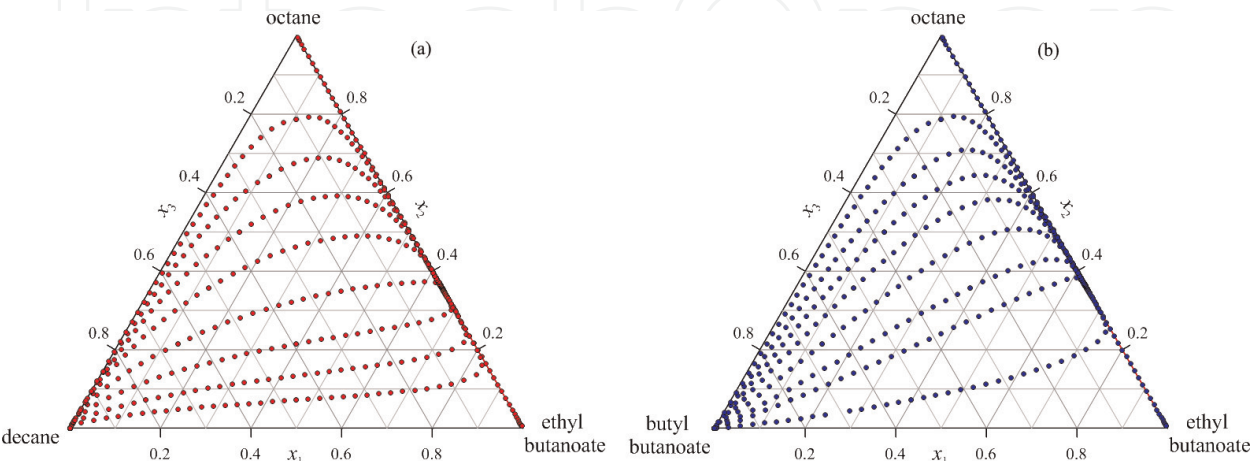


Figure 18. Residue curve map for best solvent selection for extractive distillation operation using different entrainers. (a) Decane, (b) butyl butanoate. Curves obtained with UNIFAC-DM.

need to use two columns (separation and recovery) increases the number of design criteria. Therefore, six variables have been taken to configure the first column: number of steps, reflux ratio, solvent/feed ratio, feed stage, solvent stage, and temperature of the solvent. To obtain the best conditions for the planned operation a sensitivity analysis was carried out in relation to different variables, the results of which are summarized in **Figure 19**. The solvent-feed ratio is the design variable with the most impact on the compositions of ethyl butanoate in the head and octane in the bottom, together with the energy consumption of the process. The reflux ratio largely determines the decane contents in the head.

Maximization of the ethyl butanoate composition in the head and minimization of the composition of solvent (decane) in the head, together with maximization of octane in the bottoms and the energy consumption are the main goals that must be found in the design of the extractive distillation column. The final configuration generated by the simulator is shown in **Figure 20**.

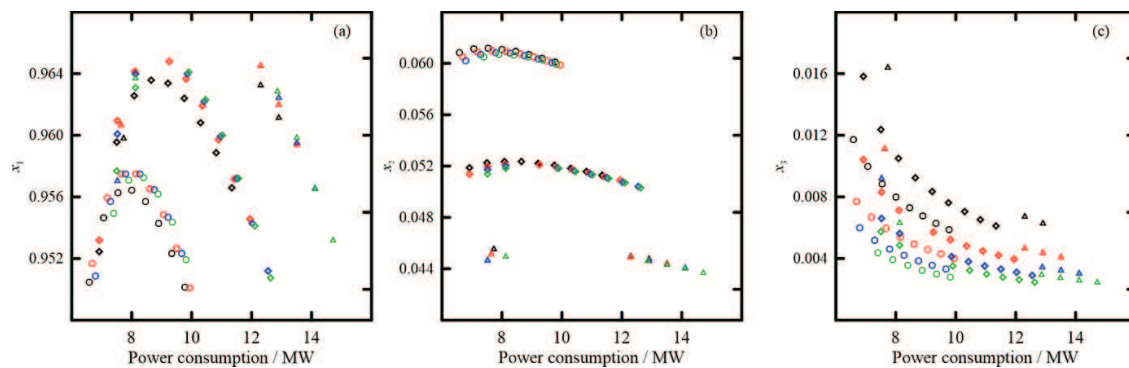


Figure 19. Sensitivity analysis curves for the following conditions: $N = 30$, $F-S = 20$ and S -Stage = 7. (o) $S/F = 5$; (•) $S/F = 6$; (1) $S/F = 7$. (—) $R = 1$; (—) $R = 1.33$; (—) $R = 1.66$; (—) $R = 2$. (a) Top composition of ethyl butanoate; (b) bottom composition of octane; and (c) top composition of decane.

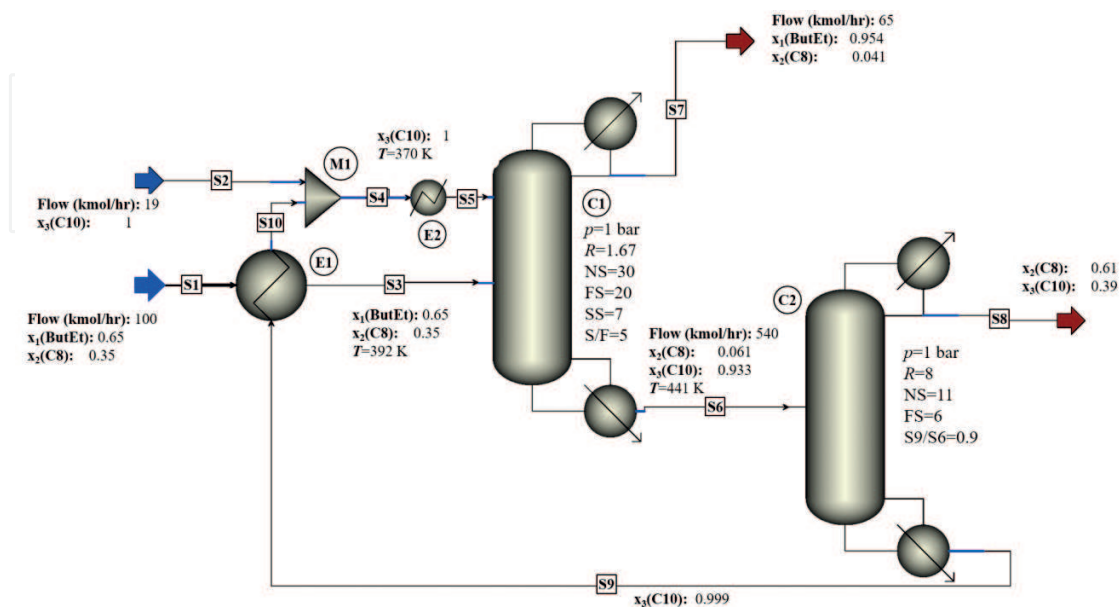


Figure 20. Simulation-scheme to separate the binary ethyl butanoate + octane by extractive distillation.

6. Conclusions

The different theoretical and practical settings related to azeotropy within the context of chemical engineering, have been described taking into account the experience of our research group in this area. The relationship between the presence of azeotropes, the non-ideality of the solution and the difference in vapor pressures of the pure compounds has been exposed. This information, together with some additional knowledge about the compounds involved in a solution, can be used to estimate the appearance of the azeotrope.

The combination of direct and indirect measuring techniques, together with suitable treatment of the results, is an excellent way to generate experimental data on which to base the studies. On the other hand, the polynomial equation proposed and used here would seem to be the best option to model the systems, provided that the parameters are optimized using all the experimental data available by means of a combined correlation procedure.

For the prediction of azeotropes, COSMO-RS method produces the best results, although in some cases the quantitative values produced by UNIFAC-DM approximate real values. Simulation of a process by *pressure-swing-distillation* and another by *extractive-distillation* allow verify the impact of the modeling and selection of the design parameters on the results of the separation operation.

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Nomenclature

ARD_f	relative deviations in absolute value ($\equiv f_{\text{exp}} - f_{\text{est}} \cdot 100/f_{\text{exp}}$)
$B_{ii}, B_{ij}, \text{m}^3 \text{mol}^{-1}$	second Virial coefficient for pure component "i" and ij-pair for mixtures
C_n	ternary parameters for molar Gibbs excess model in Eq. (18)
FS	feed stage in distillation column
$g^E, \text{J} \cdot \text{mol}^{-1}$	excess molar Gibbs function
$g_{n,N}^E$	excess molar Gibbs function given by Eq. (15)
$g_k^{(i-j)}$	coefficients for molar Gibbs excess energy model in Eq. (17) for binary i-j
G_{ij}	interaction parameters of NRTL model

$h^E, \text{J}\cdot\text{mol}^{-1}$	excess enthalpy
L	liquid phase
NS	number of stages in distillation column
p, kPa	pressure
p_i, kPa	partial pressure of i-th component
p_i°, kPa	vapor pressure of pure component i
P_N / P_j	polynomial of order N / Coefficient of polynomial P_N
R or R	gas constant $\text{Pa}\cdot\text{m}^3 \text{mol}^{-1}$ / Reflux ratio in distillation column
SS	solvent feed stage in extractive distillation column
S/F	solvent-To-Feed ratio in extractive distillation column
T, K	system temperature
u	number of carbons in alkyl substituent of esters
$v^E, \text{m}^3 \text{mol}^{-1}$	molar excess volume
V	vapor phase
x_i	molar fraction of i-th component in the solution
y_i	generic thermodynamic quantity/vapor composition of i-th component
z_i	active fraction of i-th component
Z_n	product of active fractions up to nth-component

Sub/Superscripts

est	denotes a property estimated by a model
exp	denotes an experimentally determined property
aze	relative to azeotropic conditions

Greek letters

α_{ij}	non-randomness parameter of NRTL model
δ_{ij}	function of second Virial coefficients in the mixture ($\equiv 2B_{ij} - B_{ii} - B_{jj}$)
γ_i	activity coefficient of i-th component
Φ_i	ratio between fugacity coefficient of component "i" in solution and as saturated vapor
τ_{ij}	τ -function of NRTL model
v	number of carbons in alkanols

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References

- [1] Grayson M, Kirk RE, Othmer DF. Kirk-Othmer Encyclopedia of Chemical Technology. New York: Wiley; 1984. p. 22950. DOI: 10.1002/0471238961
- [2] Ullmann F. Ullmann's Encyclopedia of Industrial Chemistry. 7th ed. Weinheim: Wiley-VCH. DOI: 10.1002/14356007
- [3] Green DW, Perry RH. Perry's Chemical Engineers' Handbook. Vol. 1973. NY: McGraw-Hill; 1973. p. 2240
- [4] Robinson CS. The Elements of Fractional Distillation. NY: McGraw-Hill; 1922. p. 216
- [5] Malesiński W. Azeotropy and Other Theoretical Problems of Vapour-Liquid Equilibrium. New York: Interscience Publishers; 1965. p. 221
- [6] Swietoslawski W. Azeotropy and Polyazeotropy. New York: Pergamon Press; 1963. p. 226
- [7] Gmehling J, Menke J, Krafczyk J, Fischer K. Azeotropic Data, Part I and Part II. Weinheim: VCH-Publishers; 1994. p. 1992
- [8] Horsley LH. Azeotropic Data I-III, ACS. Washington: ACS; 1973. DOI: 10.1021/ba-1973-0116
- [9] Blanco AM, Ortega J. Densities and vapor-liquid equilibrium values for binary Mixtures composed of methanol+an ethyl ester at 141.3 kPa with application of an extended correlation equation for isobaric VLE data. Journal of Chemical & Engineering Data. 1998;**43**: 638-645. DOI: 10.1021/je980012o
- [10] Ortega J, Hernandez P. Thermodynamic study of binary mixtures containing an isobutylalcohol and an alkyl (ethyl to butyl) alkanoate (methanoate to butanoate), contributing with experimental values of excess molar enthalpies and volumes, and isobaric vapor-liquid equilibria. Journal of Chemical & Engineering Data. 1999;**44**:757-771. DOI: 10.1021/je990004n
- [11] Ortega J, Espiau F, Postigo M. Vapor-liquid equilibria at 101.32 kPa and excess properties of binary mixtures of butyl esters+ tert-butyl alcohol. Journal of Chemical & Engineering Data. 2005;**50**:444-454. DOI: 10.1021/je0497350

- [12] Ortega J, Fernández L, Sabater G. Solutions of alkyl methanoates and alkanes: Simultaneous modeling of phase equilibria and mixing properties. Estimation of behavior by UNIFAC with recalculation of parameters. *Fluid Phase Equilibria*. 2015;**402**:38-49. DOI: 10.1016/j.fluid.2015.05.031
- [13] Ortega J, Peña J, de Afonso C. Isobaric vapor-liquid equilibria of ethyl acetate + ethanol mixtures at 760 ± 0.5 mmHg. *Journal of Chemical & Engineering Data*. 1986;**31**:339-342. DOI: 10.1021/je00045a023
- [14] Rios R, Ortega J, Fernandez L, de la Nuez I, Wisniak J. Improvements in the experimentation and the representation of thermodynamic properties (iso-p VLE and y^E) of alkyl propanoate+alkane binaries. *Journal of Chemical & Engineering Data*. 2014;**59**:125-142. DOI: 10.1021/je4009415
- [15] Ortega J, Espiau F. A new correlation method for vapor-liquid equilibria and excess enthalpies for nonideal solutions using a genetic algorithm. Application to ethanol+n-alkane mixtures. *Industrial and Engineering Chemistry Research*. 2003;**42**(20):4978-4992. DOI: 10.1021/ie030327j
- [16] Ortega J, Espiau F, Wisniak J. New parametric model to correlate the Gibbs excess function and other thermodynamic properties of multicomponent systems. Application to binary systems. *Industrial and Engineering Chemistry Research*. 2010;**49**:406-421. DOI: 10.1021/ie900898t
- [17] Fernández L, Pérez E, Ortega J, Canosa J, Wisniak J. Multiproperty modeling for a set of binary systems. Evaluation of a model to correlate simultaneously several mixing properties of methyl ethanoate+alkanes and new experimental data. *Fluid Phase Equilibria*. 2013;**341**:105-123. DOI: 10.1016/j.fluid.2012.12.027
- [18] Wisniak J, Ortega J, Fernández L. A fresh look at the thermodynamic consistency of vapour-liquid equilibria data. *The Journal of Chemical Thermodynamics*. 2017;**105**:385-395. DOI: 10.1016/j.jct.2016.10.038
- [19] Fernández L, Ortega J, Wisniak J. A rigorous method to evaluate the consistency of experimental data in phase equilibria. Application to VLE and VLLE. *AIChE Journal*. 2017;**63**:5125-5148. DOI: 10.1002/aic.15876
- [20] Pérez E, Ortega J, Fernández L, Wisniak J, Canosa J. Contributions to the modeling and behavior of solutions containing ethanoates and hydrocarbons. New experimental data for binaries of butyl ester with alkanes (C_5 to C_{10}). *Fluid Phase Equilibria*. 2016;**412**:79-93. DOI: 10.1016/j.fluid.2015.12.013
- [21] Sosa A, Fernández L, Ortega J, Pérez E. La modelización termodinámica en la simulación de un proceso de rectificación. *Revista Academia Canaria Ciencias*. 2016;**XXVIII**:7-31
- [22] Wade J, Merriman RW. Influence of water on the boiling point of ethyl alcohol at pressures above and below the atmospheric pressure. *Journal of the Chemical Society, Transactions*. 1911;**99**:997-1011. DOI: 10.1039/ct9119900997

- [23] Smith JM, Van Ness HC, Abbott MM. Introduction to Chemical Engineering Thermodynamics. 7th ed. New York: McGraw-Hill, Inc; 2004. p. 817
- [24] Bancroft WD. The Phase Rule. New York; 1897
- [25] Prausnitz JM, Lichtenthaler RN, de Azevedo EG. Molecular Thermodynamics of Fluid-Phase Equilibria. New York: Prentice Hall; 1998. p. 864
- [26] Hála E, Pick J, Fried V, Vilím O. Vapor-Liquid Equilibrium. 2nd ed. Oxford: Pergamon Press; 1967. p. 599
- [27] Raal JD, Gadodia V, Ramjugernath D, Jalari R. New developments in differential ebulliometry: Experimental and theoretical. Journal of Molecular Liquids. 2006;**125**:45-57. DOI: 10.1016/j.molliq.2005.11.015
- [28] Chen GH, Wang Q, Zhang LZ, Bao JB, Han SJ. Study and applications of binary and ternary azeotropes. Thermochimica Acta. 1995;**253**:295-305. DOI: 10.1016/0040-6031(94)02078-3
- [29] Gmehling J, Böls R. Azeotropic data for binary and ternary systems at moderate pressures. Journal of Chemical & Engineering Data. 1996;**41**:202-209. DOI: 10.1021/jc950228f
- [30] Rogalski M, Malanowski S. Ebulliometers modified for the accurate determination of vapour-liquid equilibrium. Fluid Phase Equilibria. 1980;**5**:97-112. DOI: 10.1016/0378-3812(80)80046-x
- [31] Wisniak J, Apelblat A, Segura H. An assessment of thermodynamic consistency tests for vapor-liquid equilibrium data. Physics and Chemistry of Liquids. 1980;**35**:1-58. DOI: 10.1080/00319109708030571
- [32] Van Ness HC. Thermodynamics in the treatment of (vapor+liquid) equilibria. The Journal of Chemical Thermodynamics. 1995;**27**:113-134. DOI: 10.1006/jcht.1995.0011
- [33] Redlich O, Kister AT. Thermodynamics of nonelectrolyte solutions-xyt relations in a binary system. Industrial and Engineering Chemistry. 1948;**40**:341-345. DOI: 10.1021/ie50458a035
- [34] Fredenslund P, Gmehling J, Rasmussen P. Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method. Amsterdam/New York: Elsevier; 1977. p. 379
- [35] Herington EFG. A method for testing thermodynamic consistency. Journal Institute of Petroleum. 1951;**37**:457-459
- [36] Wisniak J. The Herington test for thermodynamic consistency. Industrial and Engineering Chemistry Research. 1994;**33**:177-180. DOI: 10.1021/ie00025a025
- [37] Van Ness HC, Byer SM, Gibbs RE. Vapor-liquid equilibrium: Part I. An appraisal of data reduction methods. AIChE Journal. 1973;**19**:238-244. DOI:10.1002/aic.690190206
- [38] Van Ness HC. Precise testing of binary vapour-liquid equilibrium data by the Gibbs-Duhem equation. Chemical Engineering Science. 1959;**11**:118-124. DOI:10.1016/0009-2509(59)80006-3

- [39] Fernández L, Ortega J, Sabater G, Espiau F. Experimentation and thermodynamic representations of binaries containing compounds of low boiling points: Pentane and alkylmethanoates. *Fluid Phase Equilibria*. 2014;**363**:167-179. DOI: 10.1016/j.fluid.2013.11.026
- [40] Fernández L, Perez E, Ortega J, Canosa J, Wisniak J. Measurements of the excess properties and vapor-liquid equilibria at 101.32 kPa for mixtures of ethyl ethanoate+alkanes (from C₅ to C₁₀). *Journal of Chemical & Engineering Data*. 2010;**55**:5519-5533. DOI: 10.1021/je100832h
- [41] Fernández L, Ortega J, Pérez E, Toledo F, Canosa J. Multiproperty correlation of experimental data of the binaries propyl ethanoate+alkanes (pentane to decane). New experimental information for vapor liquid equilibrium and mixing properties. *Journal of Chemical & Engineering Data*. 2013;**58**:686-706. DOI: 10.1021/je3011979
- [42] Unpublished data measured in our laboratory
- [43] Ortega J, Sabater G, de la Nuez I, Quintana J. Isobaric vapor-liquid equilibrium data and excess properties of binary systems comprised of alkyl methanoates +hexane. *Journal of Chemical & Engineering Data*. 2007;**52**:215-225. DOI: 10.1021/je060355j
- [44] Feng L-C, Chou C-H, Tang M, Chen Y-P. Vapor-liquid equilibria of binary mixtures 2-butanol+butyl acetate, hexane+butyl acetate, and cyclohexane+2-butanol at 101.3 kPa. *Journal of Chemical & Engineering Data*. 1998;**43**:658-661. DOI: 10.1021/je9800205
- [45] Ortega J, Espiau F, Tojo J, Canosa J, Rodriguez A. Isobaric vapor-liquid equilibria and excess properties for the binary systems of methyl esters+heptane. *Journal of Chemical & Engineering Data*. 2003;**48**:1183-1190. DOI: 10.1021/je030117d
- [46] Acosta J, Arce A, Martinez-Ageitos J, Rodil E, Soto A. Vapor-liquid equilibrium of the ternary system ethyl acetate+hexane+acetone at 101.32 kPa. *Journal of Chemical & Engineering Data*. 2002;**47**:849-854. DOI: 10.1021/je0102917
- [47] Rios R, Ortega J, Fernández L, Sosa A. Strategy for the management of thermodynamic data with application to practical cases of systems formed by esters and alkanes through: Experimental information, checking-modeling and simulation. *Industrial and Engineering Chemistry Research*. 2018;**57**:3410-3429. DOI: 10.2021/acs.iecr.7b04918
- [48] Ortega J, González C, Galván S. Vapor-liquid equilibria for binary systems composed of a propyl ester (ethanoate, propanoate, butanoate)+an alkane (C₇, C₉). *Journal of Chemical & Engineering Data*. 2001;**46**:904-912. DOI: 10.1021/je000358a
- [49] Rios R, Ortega J, Fernández L. Measurements and correlations of the isobaric vapor-liquid equilibria of binary mixtures and excess properties for mixtures containing an alkyl (methyl, ethyl) butanoate with an alkane (heptane, nonane) at 101.3 kPa. *Journal of Chemical & Engineering Data*. 2012;**57**:3210-3224. DOI: 10.1021/je300799f
- [50] Sabater G, Ortega J. Excess properties and isobaric vapor-liquid equilibria for four binary systems of alkyl (methyl to butyl) methanoates with decane. *Fluid Phase Equilibria*. 2010;**291**:18-31. DOI: 10.1016/j.fluid.2009.12.003

- [51] Ortega J, Espiau F, Dieppa R. Measurement and correlation of isobaric vapour-liquid equilibrium data and excess properties of ethyl methanoate with alkanes (hexane to decane). *Fluid Phase Equilibria*. 2004;**215**:175-186. DOI: 10.1016/j.fluid.2003.08.003
- [52] Gorbunova LV, Lutugina NV, Malenko YI. Relations between the boiling points and composition in binary systems formed by acetic acid, ethyl acetate, methyl ethyl ketone and hexane. *Zhurnal Prikladnoi Khimii (Leningrad)*. 1965;**38**:374-377
- [53] Marrufo B, Rigby B, Pla-Franco J, Loras S. Solvent effects on vapor liquid equilibria of the binary system 1-hexene+n-hexane. *Journal of Chemical & Engineering Data*. 2012;**57**: 3721-3729. DOI: 10.1021/je3009599
- [54] Galvan S, Ortega J, Susial P, Peña JA. Isobaric vapor-liquid equilibria for propyl methanoate+n-alkanes (C_7 , C_8 , C_9) or n-alkanols (C_2 , C_3 , C_4). *Journal of Chemical Engineering of Japan*. 1994;**27**:529-534. DOI: 10.1252/jcej.27.529
- [55] Chen Z, Hu W. Isobaric vapor-liquid equilibriums of octane-ethyl acetate and octane-isopropyl acetate systems. *Chinese Journal of Chemical Engineering*. 1995;**3**:180-186
- [56] Ogorodnikov SK, Kogan VB, Nemtsov MS. Separation of C(5) hydrocarbons by azeotropic and extractive distillation: IV liquid-vapor equilibrium in systems of hydrocarbons and methyl formate. *Zhurnal Prikladnoi Khimii (Leningrad)*. 1961;**34**:581-584
- [57] Renon H, Prausnitz J. Local composition in thermodynamic excess function for liquid mixtures. *AIChE Journal*. 1968;**14**:135-142. DOI: 10.1002/aic.690140124
- [58] Nocedal J, Wright SJ. *Numerical Optimization*. 2nd ed. Berlín: Springer; 2006. p. 664. DOI: 10.1007/978-0-387-40065-5
- [59] Deb K. *Multi-Objective Optimization Using Evolutionary Algorithms*. New York: Wiley; 2001. p. 518
- [60] Fernández L, Sosa A, Ortega J. Multiobjective correlation of properties of binary systems using an evolutionary algorithm. Practical examples to analyze the impact of a trade-off decision on the simulation of rectification operations. *Trends in Chemical Engineering*. 2018, in press
- [61] Gmehling J, Li J, Schiller M. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Industrial and Engineering Chemistry Research*. 1993;**32**:178-183. DOI: 10.1021/ie00013a024
- [62] Klamt A. Conductor-like screening model for real solvents: A new approach to the quantitative calculation of solvation phenomena. *The Journal of Physical Chemistry*. 1995;**99**: 2224-2235. DOI: 10.1021/j100007a062
- [63] Aspen Technologies Inc. *Aspen Physical Properties System*. Cambridge: Aspen Technologies Inc; 2004

- [64] Negadi L, Belabbaci A, Kaci AA, Jose J. Isothermal vapor-liquid equilibria and excess enthalpies of (propyl ethanoate+heptanes), (propyl ethanoate+cyclohexane) and (propyl ethanoate+1-hexene). *Journal of Chemical & Engineering Data*. 2007;**52**:47-55. DOI: 10.1021/je060184i
- [65] Jimenez E, Román L, Wilhelm E, Roux-Desgranges G, Grolier J-PE. Excess heat capacities and excess volumes of (an n-alkyl alkanoate+heptane or decane or toluene). *The Journal of Chemical Thermodynamics*. 1994;**26**:817-827. DOI: 10.1006/jcht.1994.1098

